THE GLASS INDUSTRY

VOLUME 22, NUMBER 3, MARCH, 1941

# INSPECTION METHODS AT DIAMOND GLASS COMPANY

**A six year program of modernization has brought this factory the latest in glass house equipment, with a high degree of operating efficiency. The ratio of rejected ware, however, still remains higher than for most plants, which is due to the management's belief in a very rigid system of inspection.**

As the result of a continuous program of modernization that has been going on for more than six years, Diamond Glass Company is today one of the most efficient of the smaller plants in the entire industry. Starting at the melting operation, every department, year by year, has been subjected to the scrutiny of the most experienced engineers. Today, batch handling system, forming machines, lehrs and inspection departments are considered the last word for the particular service required of them.

Quite unique among glass houses is the inspection and packing departments. Not that the company has pulled any rabbits from its hat or evolved new and revolutionary methods; but the completeness of the system and the degree of its efficiency is noteworthy. Proof of this is to be seen from the fact that the average of ware thrown out or discarded due to defects is as high as 20 per cent. The company has set up rigid standards, so that a minimum of bad ware will escape the inspection system. Under this standard it is realized that bottles are rejected which to some, might be commercially accepted, but it prefers to err on the conservative side.

Inspection and packing is carried out at the ends of the lehrs under two adjustable fluorescent 48″, three tube, lighting units, one to each side of the lehr. The inspectors (who in some cases are also the packers) work in shifts; the two day shifts are women, and the night shift is composed of men. The inspectors employed on any job vary from two all the way up to eight, depending on the type ware and its size. Each bottle is plugged and gaged with a throat gage for opening and finish and then is inspected for defects. If it passes this in-

**Fig. 1. (right) View of packing and inspection departments showing two of the lehrs. Note the overhead conveyor system handling empty cartons. Lighting is supplied to each lehr by two adjustable units of three tube fluorescent lights.**

**Fig. 2. (below) Preliminary inspection of bottles.**

**Fig. 3. Another inspection station showing overhead conveyor for empty cartons and cullet hopper.**

**Fig. 4. (upper left) Throat gauges being used in quart bottles.**

**Fig. 5. (above) Using bottom gauges on round bottles for outside dimensions.**

**Fig. 6. (left) Inspector using outside gauge. Girl in background is using throat gauge and thread gauge.**

**Fig. 7. Cut-off saw in laboratory showing ring samples in the background.**

spection, it is then gaged for outside dimensions and packed. Most of the ware is cap gaged. G. C. A. and Preston techniques are employed in the inspection of all ware. The inspection is very careful and all tests are made in excess of the requirements in order to give the customer a more perfect product. Rejects are put to one side and are checked later by a shift foreman.

The inspectors put their number on each carton filled. The inspectors reports are handed in to the shift foreman each day and the reports are filed and averaged up and placed on the bulletin board for every one in the plant to inspect. This report sheet lists the inspectors names and averages as to their standing. By listing these averages, any person in the plant can find the standing of the inspection group.

Mold changes require a slip to be filled out giving the reasons for changing and sent with a sample bottle to the superintendent. If a single mold is changed, a report is sent from the blowing room to the inspectors, and for them to be on the lookout for that particular mold number. Two copies of this report are made and sent to the mold shop and to the inspection department. The report gives the number of the mold, the time taken off, the shift number and the reason. The new mold ware is then checked for weight of glass, fill point, capacity, etc., before the bottle is accepted for packing.

Reinspection is carried on by two men who pick random boxes of ware from the different inspectors. Twenty-four boxes are taken, which averages one dozen bottles from each inspector. This random inspection is carried out every day. At night the boxes are collected and piled to one side for the day men to check. On a 24 hour basis, one bottle is taken from each mold each hour and the weights are recorded. The bottles are tested with the polariscope every two hours. (Four from each lehr, each mold.) Pressure ware is pressure tested at 350 pounds every three hours. One bottle from each mold, each lehr, is tested for weight, capacity, polariscope, thermal, and ring section in the laboratory. In cutting the ring sections, the round bottles are cut with and against the seam. All other bottles are cut across the shoulder and bottom as well as with and against the mold seam. This is done once a day except on a new job. When trouble is found, the hot end (blowing room) is advised and when the trouble is corrected, the corrected bottles are re-cut.

Twice a week, sample bottles are sent to the Hartford-Empire Company for testing. The report from Hartford covers annealing, homogeniety, specific gravity, chemical composition and the apparent temper of side and bottom. When trouble is encountered, the ware is sent to the Preston Laboratories for checking.

Shipping cartons in all instances are supplied by the customers and are shipped into the plant flat. They are

Fib. 8. Checker placing filled cartons on a pallet for removal to warehouse.

Fig. 9. (right) Carton sealer with automatic system which tells which conveyor is low on cartons.

Fig. 10. Looking down on the empty carton conveyor distribution center in the warehouse.

Note. The arrows point to the warning lights and to the manually operated switches at the carton sealing machine.

made up on one of two carton making machines in the warehouse adjoining the inspection. One machine is a top sealer and the other is a bottom sealer. The made-up cartons go up a rubber belt-conveyor to a level above the inspection stations in the warehouse and by means of switches, branch off to the five lehrs. These switches are hand operated and are located at the carton making machine, and by means of these, the cartons can be directed to any one of the lehrs. At the carton making machine is a row of lights which flash on to warn the carton makers when the cartons to any one lehr have reached a minimum number. There is also a carton stitcher for cartons that have to be wire stitched.

The filled cartons at the ends of the lehrs are placed on a short conveyor and from there are placed on pallets by the checker. When these pallets are filled, they are moved to the warehouse by means of one of two gasoline driven Towmotor fork lift trucks. The cullet hoppers are also removed by the Towmotors. The cartons were formerly moved by small four wheeled trucks and were pushed by hand. The Towmotor and pallets have been used since January of 1940 and shipping and cullet removal has been greatly speeded up by their use. The warehouse stacking is done much more quickly and easier as the lift trucks will stack four pallets high, thus saving in warehouse space. Motor freight trucks can now be loaded in 35 minutes using one man on the lift truck and two men to unload the pallets and load the truck. Freight cars are loaded in the same way, but using four men to load and unload. The plant is in a unique location, being situated between the Reading and the Pennsylvania railroads. The incoming materials are brought in by the Reading and the outgoing on the Pennsylvania and by motor freight, which arrangement provides a continuous steady flow of straight production, from raw materials received to finished goods. Since the management operates the company on an engineering basis, naturally engineering principles were applied to the problem of inspection and packing, as it was felt that not enough emphasis was placed on the inspection end of the business by the industry as a whole.

Fig. 11. A view looking up at the carton conveyors in the warehouse.

# ANTI-TRUST SUIT GOES TO TRIAL

Trial of the Government suit charging conspiracy to violate anti-trust laws, which has been in and out of court for many months, began before Judge Frank L. Kloeb in the Federal District Court of Toledo, Ohio, on March 3rd at 10 a.m.

F. G. Smith, President of the Hartford-Empire Company took the stand as the first witness and indications were that he would continue to occupy the witness chair for several days.

The Government won the first round in the case when Judge Kloeb ruled that letters and documents segregated from the files of the defendant corporation are admissible as evidence. The defense attorneys say that many thousands of letters have been taken from the files of their client since the Government investigation which began with the hearing before the Senate Temporary National Economic Committee in 1938. Samuel S. Isseks, who is the Government's chief attorney, said that his case will be presented largely by document.

Unlike the previous times when the parties have come before Judge Kloeb, there was no doubt on the morning of March 3rd as to what would happen. Judge Kloeb had ordered on February 14th that the defendant be ready for trial when the court met again after its next adjournment. Since that time there have been no additional conferences between attorneys for the defendant and the Government regarding settlement.

On numerous occasions, earlier, it seemed certain that the case would reach a solution out of court. A consent decree had been drawn and most of its features had been agreed to. In addition another plan for the reorganization of the glass industry to the satisfaction of the Government was under consideration. However, when the attorneys came into court on February 14th it was reported that new demands had been made by the small licensees of the Hartford-Empire Company, some of them not being defendants in the case. It is understood that the licensees demanded that certain patents owned by Corning and Hazel-Atlas should be thrown into the new pool of patents to be known as The Glass Institute. The Government backed these demands, and the attorneys for Corning and Hazel-Atlas figuratively threw up their hand and said "enough."

Attorneys for both the firms told Judge Kloeb at the February 14th conference that in order to reach a settlement out of court they had agreed to things which no court would ever require of them, but that with the added demand now being made, trial of the case was preferred to negotiation.

The scene in the courtroom at the final February conference was dramatic in the extreme. Judge Kloeb, obviously surprised and disappointed, called for the first witness to be sworn. An unusual situation, however, then presented itself. Corning had been forced to assign a new attorney to the case because of the withdrawal of John Lord O'Brian as its general counsel. Mr. O'Brian had been called into Government service as general counsel for the Office of Production Manager at the request of Mr. Knudsen, Defense Commissioner. It developed that in giving up the services of Mr. O'Brian, Corning had been assured that the Department of Justice would not press the quick trial of the anti-trust suit. Mr. Isseks was obliged to read to the court a communication received by him from Thurman Arnold, head of the anti-trust division, instructing him to consent to a delay not to exceed 30 days.

From the first days testimony it was obvious what course the Government would pursue in the presentation of its case. After the preliminary questioning, in which Mr. Smith identified himself, Mr. Isseks turned to a comparison of the glass manufacturing industry in 1910 and 1911 with today. The Government attorney succeeded in getting the witness to admit that in the early days there were competing firms in the glass industry, and also to testify that today Hartford-Empire licensees manufacture about 67 per cent of the glass in the container field.

Mr. Smith testified that some 3 or 4 per cent of the glass containers manufactured today are made by firms not licensed by Hartford-Empire or Owens Illinois. He said that as early as 1911 the firm had begun to study means of perfecting automatic glass making machinery.

Defense attorneys objected strenuously and upon many grounds when Mr. Isseks began presenting the witness with copies of letters and documents for the purpose of identification. Judge Kloeb, however, ruled that the copies should be admitted. Some of the letters and memoranda were between Mr. Smith and William H. Honiss, former official of the firm who, though named as a defendant in the suit, has since died. The documents in question dealt with the negotiations in 1919 for the then proposed merger of the Hartford-Fairmont Company, Corning Glass Works and the Empire Machine Co.

One of the things of which Mr. Smith admitted the authorship included an opinion written by him that the consummation of this proposed merger might result in the domination of certain potential competitors. Certain assets of the Hartford-Fairmount Company might be useful, Mr. Smith wrote in 1919, in limiting competition.

Defense attorneys contend that many of the contracts to which the Government objects and upon which it relies through this case are no longer in effect and therefore are not possible evidence in the case.

The trial was resumed on March 4th. A long drawn out and bitterly contested suit is expected by both sides.

### DONALD M. SMITH

Mr. Donald M. Smith, president of the McKee Glass Company, Jeannette, Pa., died suddenly of a heart attack at his home February 26. Mr. Smith's death followed by only seven months that of his older brother, Maurice A. Smith.

A native of Fostoria, Ohio, Mr. Smith was a graduate of Cornell University. In 1915, he become associated with the McKee Glass Company and served as vice president for many years until his elevation to the presidency last summer.

• Dr. H. H. Blau has resigned from the research department of the Corning Glass Works to accept a position in the production department of the Federal Glass Company, Columbus, Ohio.

# DISCUSSION AND ABSTRACTS OF PAPERS TO BE PRESENTED AT THE BALTIMORE MEETING

During the annual meeting of the American Ceramic Society, which this year is being held in Baltimore the week of March 30, the Glass Division will conduct its customary technical and business sessions. The program to be presented reflects the careful work of A. K. Lyle and W. C. Taylor, and the total of twenty-two papers they have arranged will extend to capacity the four half-day sessions alloted to them.

A number of the papers deal with the subject of color. Badger and Ottoson, University of Illinois, have exposed iron-bearing glasses to several sources of short wave radiation, and they report on the color changes produced. That iron in glass affects light is not news; but when light affects iron, that is news; although one might guess from the behavior of blue print paper. The time-worn topic of amber glass is treated by Moore and Scholes, N. Y. State College of Ceramics at Alfred, who seem to have tried to produce a sweeter color by the use of sugar. In the field of opal glasses, Kreidl and Weyl of Penn State College have made quite a study of phosphates. These seem to behave after the manner of vitamin $B_1$ in producing apatites, or are we thinking of something else. Of peculiar interest are the aluminum phosphate glasses made without silica, and the use of compounds of phosphorus as reducing agents.

Dasher and Ralston, Bureau of Mines, will describe a method for cleaning glass sands which seems to be practically a laundering process. It is a long time since any improvement was made in treating this important raw material, and this paper should be very interesting. Brownell and Scholes, N. Y. State College of Ceramics, will describe experiments on the mixing of sand with other glass-making materials.

Several varieties of artificial weather have been used by Owens and Emanuel, Armstrong Cork Co., in studying the weathering of bottles. In this way they saved traveling from Louisiana to Arizona. A. Herman, Seagram and Sons, uses the still more brutal autoclave test and finds out the influence of the factors of time, temperature and purity of distilled water necessary to make the tests reliable. Owens and Emanuel, similarly, resort to the high speed of the autoclave test for durability and the two papers should furnish some up-to-date checks on this method. Liebmann and Rosenblatt, Schenley Distillers Corp., present a method for testing surface alkalinity. The problem of flaking is again handled, and, very appropriately, alcoholic liquids are used for the accelerated tests. This group of papers should be of particular interest to those who attended the Fall meeting of the Division.

After a period of neglect, the interesting subject of gases dissolved in glass has been taken up, this time by Shadduck and Van Zee, Owens-Illinois Glass Company. These almost imaginary items will be made real and present by their exposition. J. C. Turnbull, Preston Laboratories, whose work on the identification of cords by separation of fine glass powders by density differences made such a stir at Hershey, will present a startling method for making the relative position and distribution of the centrifuged particles visible by stroboscopic light. Another opportunity for debate on the origin of these cords will undoubtedly arise.

No fewer than seven physical properties of glasses, as modified by the addition of barium oxide and zinc oxide, will be discussed by the representatives of the General Research Lab., Owens-Illinois Glass Co. This work is in line with the modern trend toward improving our comparatively simple soda-dolomite-silica glasses by small additions of extra bases. Sun and Silverman, University of Pittsburgh, have made a glass suitable for the mythical cup of Tantalus himself in their glass made up of $K_2O$, $Ta_2O_5$ and $SiO_2$.

Some rugged specimens of vitreous mathematics have been prepared by Nelson W. Taylor, Penn State College, in his further study of elastic after-effects and dielectric absorption in glass. More complete theories concerning the internal architecture of glasses has been prepared by B. E. Warren, M.I.T., as a result of his extended X-ray studies on glasses. J. Biscoe, of the same department, has carried these X-ray defraction studies into the investigation of soda-lime-silica glasses, whose intimate atomic geography he is now ready to map with a certainty extending to fractional angstrom units. Potassium borate glasses, not hitherto investigated to any extent, have been studied by R. L. Green, Research Lab., General Electric Co. This work seems to throw some light on the anomalous behavior of the potassium borate glasses which is to be explained by inferences drawn from the X-ray patterns.

The utilization of flat-glass products will be discussed by R. A. Miller, Pittsburgh Plate Glass Co., who is in an excellent position to outline the multitude of ways in which glass becomes vitally important in plates and sheets. In the event that some of us find it difficult to tell the difference between plate and window glass, we shall be taught how, by Adams and French, Mellon Institute, who use interference patterns for this identification. Apparently one of these is flat and the other is nearly flat.

The various things that may happen to a bottle when it is being filled with a beverage containing dissolved $CO_2$ under pressure will be set forth by John A. Sharf of Washington, D. C. We are likely to find that our bottles get something more shocking than the mere application of gradually increasing pressure.

These twenty-two papers have been cleverly arranged on the time schedule so that Tuesday forenoon is largely devoted to the durability problem, Tuesday afternoon is given to the papers on dissolved gases, cords and phosphate crystals, and the first two papers on Wednesday morning are the practical ones on barium and zinc glass and flat glass utilization. The X-ray papers occupy the remainder of Wednesday forenoon, and in the early afternoon, following three papers of the plant or practical type, the new glass, the foray into mathematics and the sheet-glass-sleuthing paper wind up the program. Abstracts of all papers are given beginning on page 106.

## TUESDAY MORNING, APRIL 1

**9:30-9:55 A.M.**

**1. Effect of Light on the Color of Iron-Bearing Glasses.** *By A. E. Badger and A. Ottoson, Department of Ceramic Engineering, University of Illinois, Urbana, Ill.*

Various glasses containing small amounts of iron oxide were exposed to light from a carbon arc and from a quartz-mercury arc and also to sunlight and X-rays. A study was made of the color changes that occurred, using a spectrophotometer.

**10:00-10:20 A.M.**

**2. New Methods of Cleaning Glass Sands.** *By John Dasher and Oliver C. Ralston, Nonmetals Division, U. S. Bureau of Mines, College Park, Md.*

A discussion is presented of the various forms of iron-bearing impurities in glass sands and methods for the removal of each type of impurity, with emphasis on the attrition scrubber, froth flotation, and agglomeration. The equipment and operating items that make up costs are listed, and detailed results of various treatments on different sands are included.

**10:25-10:50 A.M.**

**3. Effect of Storage Conditions on Weathering and Chemical Durability of Commercial Glass Containers.** *By J. S. Owens and E. C. Emanuel, Armstrong Cork Company, Lancaster, Pa.*

Flint bottles of different chemical compositions were stored empty, capped and uncapped, for periods up to twelve months at (1) 100°F., 80% relative humidity; (2) 130°F., 10% relative humidity; and (3) normal room temperature and humidity. The effect of storage was determined by visual examination and by tests of the alkali extraction by water at 50° and 120°C. Photomicrographs of weathered bottle surfaces were made. Important factors in the weathering and chemical durability of empty, commercial glass containers stored under these conditions are discussed.

**10:55-11:05 A.M.**

**4. Factors Influencing Autoclave Chemical Durability Tests of Glass Containers.** *By A. Herman, Joseph E. Seagram & Sons, Incorporated, Louisville, Ky.*

Various factors affect the results obtained in the autoclave chemical durability tests, such as the time and temperature of extraction and impurities in the distilled-water leaching medium. These factors are discussed with particular emphasis given to distilled-water impurities. Glass containers of a wide range of durability were tested, using water containing various known impurities. The effects on the results are listed in tables. Conclusions are drawn as to the degree of standardization of time, temperature, and purity of distilled water necessary to obtain uniform results with the test.

**11:10-11:30 A.M.**

**5. Investigation of Variable Factors in Accelerated Autoclave Chemical Durability Tests.** *By J. S. Owens and E. C. Emanuel, Armstrong Cork Company, Lancaster, Pa.*

An investigation was made of certain factors which influence the reproducibility of autoclave chemical durability tests. These factors include the method of preparation and the purity of the water used, the rinsing procedure, the volume of solution used, and variations in the test temperature and in the duration of the different periods of the heat cycle. The effect of the internal area of the container on the test result was determined, and suggestions are presented for increasing the reliability of the tests.

**11:35 A.M.-12 M.**

**6. Mehod of Testing Surface Alkalinity of Glass Bottles.** *By A. J. Liebmann and M. Rosenblatt, Schenley Distillers Corporation, New York, N. Y.*

(1) A description is given of a reliable and reproducible analytical method for testing the small amount of alkali derived from the glass by titration. (2) The magnitude and type of extraction of various commercial glasses by neutral alcoholic liquids during the accelerated test is determined, and a method of sealing alcoholic liquids in bottles during tests run above the boiling point is described. (3) The conditions of the test are determined for extracting alkali of the same order of magnitude as in (2), using water as a leaching medium. (4) A correlation of the results on accelerated tests with visible flaking phenomena is presented, and (5) the effect of the size of the glass container on the magnitude of extraction is noted.

## TUESDAY AFTERNOON

**2:00-2:30 P.M.**

**7. Analysis of Gases Dissolved in Glass and Gases Present in Seeds.** *By Hugh A. Shadduck and Arthur Van Zee, Owens-Illinois Glass Company, Toledo, Ohio.*

The procedure for analyzing gases dissolved in glass is described and some typical results for flint glass are shown. A brief account of the micromethod for determining gases present in seeds is presented together with some of the data obtained.

**2:35-2:50 P.M.**

**8. Cord Analysis.** *By J. C. Turnbull, Preston Laboratories, Butler, Pa.*

In the separation of fine glass powders according to density differences, greatly improved results are obtained by means of a stroboscopic light so that the position and motion of the glass particles in the suspending liquid can be seen while the centrifuge is in motion. The density spread of the powder and a curve giving the distribution in density may thus be obtained rapidly. This procedure is valuable as a quick check on glass quality.

The technique of obtaining separated samples has been improved, and these samples have been analyzed chemically with interesting results. Generalizations from data up to the present time indicate that the majority of cords in bottle glass, which appear conspicuous and under considerable strain in the polariscope, are batch cords and do not have their origin in aluminous refractory solution.

**2:55-3:15 P.M.**

**9. Formation of Apatites in Opal Glasses and Bone China.** *By Woldemar A. Weyl, Department of Ceramics, Pennsylvania State College, State College, Pa.*

The formation of apatite minerals is discussed and it is shown that apatites form a phosphate opal glass. On this basis, the characteristic properties of this group of opal glasses can be understood. Suggestions are made how to overcome difficulties in the production of phosphate opal glasses, especially those of the heat-resisting type. In connection with this problem, the translucency of bone china is examined.

**3:20-3:35 P.M.**

**10. Phosphate Glasses and Some Characteristic Properties.** *By N. J. Kreidl and W. A. Weyl, Department of Ceramics, Pennsylvania State College, State College, Pa.*

The properties of pure phosphate glasses as base glasses, especially those for colored oxides, are discussed. Considering the influence of alumina on the resistivity of phosphate glasses in many new applications outside of the optical field, aluminum-phosphate glasses were studied in various combinations. Glasses containing up to over 90% of aluminum phosphate and no monovalent fluxes, or, in many cases, no bivalent fluxes, could be obtained within the range of normal melting temperatures. The structure of crystalline aluminum phosphate with its striking similarity to the quartz structure offered a significant subject of comparison. The potential uses of glasses and fluxes in the electrical industries are examined in connection with the characteristic properties of aluminum-phosphate glasses. Of other phosphate glasses of similar type, iron-phosphate glass seems to be of primary interest.

3:40-3:55 P.M.

**11. Phosphorous Compounds as Reducing and Fining Agents for Glasses.** *By W. A. Weyl and N. J. Kreidl, Department of Ceramics, Pennsylvania State College, State College, Pa.*

The usual fining agents are based on the evolution of oxygen at high temperatures and therefore cannot be applied to glasses to be melted under reducing conditions. Phosphorous and phosphides have been found to be suitable fining agents for heat-absorbing and copper-ruby glasses. These agents reduce and fine the glasses simultaneously.

## WEDNESDAY MORNING, April 2

9:30-9:55 A.M.

**12. Effect of (a) Barium Oxide and (b) Zinc Oxide on Physical Properties of a Typical Soda-Dolomite-Lime-Silica Glass.** *Owens-Illinois Glass Company, Toledo, Ohio.*

To a base glass containing 14% of sodium oxide, 12% of dolomite lime, and 74% of silica (1) barium oxide and (2) zinc oxide were systematically substituted for (*a*) $Na_2O$, (*b*) CaO + MgO, and (*c*) $SiO_2$ in amounts of 1, 3, and 5%. The effects of these substitutions on such physical properties as liquidus temperature, viscosity, deformation temperature, density, fiber softening point, coefficient of expansion, and on the resistance of the glasses to dilute acid and distilled water are presented.

10:00-10:15 A.M.

**13. Resume of Utilization of Flat Glass Products.** *By R. A. Miller, Pittsburgh Plate Glass Company, Pittsburgh, Pa.*

10:20-11:05 A.M.

**14. Summary of Work on Atomic Arrangements in Glass.** *By B. E. Warren, Massachusetts Institute of Technology.*

The present picture of the atomic arrangement in glass has developed from four kinds of information, namely, (1) laws of crystal chemistry, (2) X-ray diffraction study of glass, (3) various measured physical propetries of glass, and (4) kinds of materials and the ranges of composition in which glassforming properties exist. X-ray diffraction studies establish the predominant type of bonding in the glass; for example, the tetrahedral bonding in silicate glasses. Secondary structural features, such as those which change with annealing or conditioning, do not show up in the X-ray pattern. Most of the proposed structures are those which are suggested and partially substantiated by X-ray studies, which fit the laws of crystal chemistry and which seem best able to explain the physical properties of the glass.

The preliminary theory of immiscibility in glass systems has been extended to include a study of the temperature dependence. A consideration of thermal expansion in terms of the number of glassforming bonds allows a simple correlation between thermal-expansion coefficients in the silica-boric oxide and the soda-boric oxide systems. The same kind of considerations as those used in discussing immiscibility may be used to give a quantitative treatment of the change in coordination number of the boron atom when borci oxide is present with soda.

11:10-11:30 A.M.

**15. X-Ray Diffraction Studies of Some Soda-Lime-Silica Glasses.** *By J. Biscoe, Massachusetts Institute of Technology.*

Three soda-lime-silica glasses have been studied by the Fourier integral method. The compositions (by weight) are as follows:

| $SiO_2$ | $CaO$ | $Na_2O$ |
|---|---|---|
| 0.683 | 0.206 | 0.109 |
| .763 | .124 | .114 |
| .694 | .102 | .202 |

The radial distribution curves of the three compositions are similar. The first, and only, peak which is resolved occurs at about 1.62 a.u. This distance corresponds to the silicon-oxygen distance. The area of the peak indicates that there are four oxygens about each silicon. The remaining peaks on the curves are not resolved. A peak would be expected, however, at 2.65 a.u. corresponding to the distance between oxygens of the same silicon-oxygen tetrahedron. The area of this peak can be calculated from the composition of the glass. A peak would also be expected at about 2.7 a.u. owing to the sodium-oxygen distance. The area of this peak would be expected to correspond to about 6 oxygens around a sodium, as was found in soda-silica glass. If these two peaks are drawn on the radial distribution curves, there remains a peak whose area corresponds roughly to 7 oxygens about a calcium and which occur at about 2.4 a.u.

The interpretation of these distribution curves, although not so unequivocal as were those of the single component or even the binary glasses, leads to the same sort of picture of the atomic arrangements. Each silicon is surrounded by 4 oxygens. Some of the oxygens are bonded to 2 silicons and the remainder to but one. This forms a continuous random network with rather large holes in which the calcium and sodium ions are located.

11:35-12.00 M.

**16. X-Ray Diffraction and Physical Properties of Potassium Borate Glasses.** *By Robert L. Green, Research Laboratory, General Electric Company, Schenectady, N. Y.*

The data from X-ray studies and from measurements of physical properties of potassium borate glasses in the composition range from 0 to 40% by weight of $K_2O$ are presented. Calculations based on the X-ray diffraction patterns show a change from three- to four-fold coordination with an increase in $K_2O$ content. At a $K_2O$ content of between 20 and 25%, the coefficient of thermal expansion is a minimum, showing that the majority of the boron atoms are in four-fold coordination. The curves of composition versus transformation point, softening point, density, and refractive index show a change in slope in the composition range of 20 to 30% of the $K_2O$.

It is concluded that the random structure picture as well as the tendency for boron atoms to assume tetrahedral coordination in alkaline borate glasses satisfactorily explains both the X-ray diffraction curves and the otherwise anomalous physical behavior of the potassium borate glasses.

## WEDNESDAY AFTERNOON

2:00-2:15 P.M.

**17. Conditions Encountered During the Filling of Pressure Ware.** *By John A. Sharf, American Bottlers of Carbonated Beverages, Washington, D. C.*

Many beverages contain dissolved $CO_2$ held in solution by pressures above atmospheric. To fill these products into pressure ware calls for mechanical systems which operate at pressures above atmospheric. The bottles are thus subjected to varying conditions of internal pressure during their filling. Because the ware is usually warmer than the product, there may also be some thermal effect. The action of the filling machine and the closure application also introduces some mechanical loading. The extent and timing of these conditions depend somewhat on the type of filling apparatus, but general limits can be stated to give some consideration as to the service demands on the ware during this particular operation.

2:20-2:35 P.M.

**18. Glass Batch Mixing.** *By Wayne E. Brownell and S. R. Scholes, New York State College of Ceramics, Alfred, N. Y.*

Laboratory methods of mixing, sampling, and analyzing batches are discussed. The idea of segregation by continued mixing is shown to be fallacious. The effect of powdered materials is shown as an improvement in the rate and thoroughness of mixing.

2:40-2:55 P.M.

**19. Amber Glass and the Role of Carbon.** *By Henry Moore and S. R. Scholes, New York State College of Ceramics.*

Melting experiments, employing batch materials free

from sulfur and pure carbon in the form of sugar, demonstrate that carbon is not retained as a colorant. The value of carbon as a reducing agent in sulfur-bearing batches is confirmed, and the effect of iron is experimentally shown.

3:00-3:15 P.M.

**20. Tantalum Glass: $K_2O$—$Ta_2O_5$—$SiO_2$ Series.** *By K.-H. Sun and Alexander Silverman, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.*

The partial molal volume and refractivities, based on the Gladstone-Dale and the Lorentz-Lorenz formulas of potassia-tantala-silica glasses, have been evaluated from the experimental data of density and refractive index. Equations and constants are available for the calculation of volume and refractivities from composition, and the density and refractive index may therefore be computed. The interionic distances of Ta-O, Si-O, and K-O, calculated from the refractivity data, agree favorably with known measured values. Tantala, as compared with silica and phosphorous pentoxide, is a poor "network former." The high oxygen-to-tantalum ratio and the relatively large Ta-O distance result in the formation of new singly bonded oxygens and a glass that is loose in structure. The range of composition, which was limited by a fixed melting temperature (1400°C.), extends from 21 to 38% of potassium oxide, 5 to 36% of tantala, and 39 to 71% of silica.

3:20-3:35 P.M.

**21. Elastic After-effects and Dielectric Absorption in Glass.** *By Nelson W. Taylor, Department of Ceramics, Pennsylvania State College, State College, Pa.*

Von Schweidler's theory of dielectric absorption and Taylor and Doran's theory of the delayed elastic effect in glasses are shown to be mathematically of the same form and to lead to the same conclusions regarding the constitution of glass. They are also in accordance with the "random network" picture of glass as based on X-ray diffraction studies. The intimate relation, in the molecular sense, between the elastic and dielectric phenomena is demonstrated, and an explanation is offered for the "principle of superposition" as applied to these phenomena.

3:40-4:00 P.M.

**22. Characteristic Interference Patterns of Plate and Window Glass.** *By F. W. Adams and P. W. French, Mellon Institute, Pittsburgh, Pa.*

A simple laboratory procedure has been developed for quickly distinguishing window glass from plate glass by means of interference patterns with monochromatic illumination. Small samples may be readily identified. Commercial samples of plate and window glass have been examined by this method, and representative patterns are presented.

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## CONCERNING THE DEFINITION OF GLASS

In THE GLASS INDUSTRY for February, 1941, page 64, appear a number of suggestions for a definition of glass. Most of these definitions consist of very cautious poking of the thing with a long stick, in the evident expectation that it may bite them. This is no doubt because at heart, everyone knows that glass is a lobster[1], in Cuvier's sense of the word, and the various long-range pokings have to be cautious.

Morey agrees with the lobster definition, provided it is specified that the lobster is undercooled.

A distinguished Frenchman suggests that the French equivalent would be "homard glacé." While this suggestion is made with a very straight face, as befits a serious subject, we strongly suspect our friend of indulging in pleasantries. The joke, if joke it be, is a multiple pun. For while "glacé" normally means "frosted" or "frozen," and may be taken as the equivalent of "undercooled," "glace" may mean either ice or plate glass and "glacé" may even be a pun on the English word "glassy," so that our friend may be saying "Le verre est un homard glacé —Verre (glass is a glassy lobster)." Worse than that, there was some hint of a vowel change towards "glissé," indicating that glass was a "slippery" lobster.

However, all of these possibilities remain truthful and easily grasped, which is more than can be said of the cautious definitions in THE GLASS INDUSTRY for February.

Another definition which has much to recommend it is this: "Glass is that, which if there were none, we should have to make bottles of something else," probably goat skins. Now this as palpably true, unless it be assumed that in the absence of glass we should not make bottles at all. Such an assumption would be contrary to human nature, for man and his bottle are not soon parted. In childhood, the milk bottle is his steady companion: in callow youth he graduates to the gin bottle, which leads inevitably to the medicine bottle for the rest of his life.

—*F. W. Preston*

[1]GLASS INDUSTRY, June, 1933.

• Friends of Dr. Ing. Vaclav Ctyroky, Director of the Glass Research Institute at Hradec Kralove, Bohemia, will be glad to have news from him. THE GLASS INDUSTRY has received a letter, dated December 24, addressed from the Institute in which he conveys his cordial Christmas greetings to the ceramists in the United States.

## TECHNOLOGISTS SOUGHT BY U. S.

The U. S. Civil Service Commission has announced an open competitive examination to secure Technologists for National Defense work. Difficulty is being experienced in filling positions in such branches of technology as explosives, fuels, plastics, rubber, minerals, and textiles. Persons qualified in these branches are particularly urged to file application. Applications will be rated as received until December 31, 1941.

The positions to be filled are in several grades with salaries ranging from $2,600 to $5,600 a year. Competitors will not be given a written test, but will be rated upon their education and experience. Further information and application forms may be obtained from the Secretary of the Board of U. S. Civil Service Examiners at any first- or second-class post office, or from the United States Civil Service Commission, Washington, D. C.

In connection with the National Defense program, the Commission has also announced an examination to fill the position of chemist-petrographer. The salary is $3,200 a year, less a 3½ per cent deduction toward a retirement annuity. Applications must be on file with the Commission's Washington office not later than March 3 and March 6, 1941. The extra time is allowed those sent from Colorado and States westward.

• Mr. R. L. Shute has become associated with the Research Department of the Owens-Corning Fiberglas Corporation at Newark, Ohio. Mr. Shute has been connected with the Department of Ceramic Engineering of the University of Illinois and has contributed a number of valuable papers to the glass literature of the United States

# IMPROVING DURABILITY OF GLASS SURFACES BY TREATMENT WITH VOLATILE SALTS

By A. E. BADGER and R. R. ROUGH*

Measurement of the chemical durability of glass usually consists in determining the amount of material dissolved from the surface of the glass by any desired chemical reagent, as water, alcohol, acid, or alkali of definite concentration. Since the compositions of most commercial glasses have been fixed within small limits to produce fairly resistant glasses of suitable melting and working qualities—as well as resulting from low-cost glass batches—it is possible that improvement of the durability of glasses may be accomplished at less cost by treating the surface of the finished ware, rather than by melting glasses of special compositions. Such treatment may produce glassware which is cased with a thin layer of a more resistant glass composition.

Experiments of an exploratory nature have been made recently using the set-up shown in Figure 1, in which a soft glass rod of poor durability was placed in a tube of hard glass which extended through the end of a tubular electric furnace. A known temperature gradient thus existed over the length of the glass rod and the reaction of various vapors with the glass could be readily obtained by introducing them into the tube. Some preliminary experiments with this apparatus dealt with the action of the vapors of various metallic chlorides on the glass test rod and since the results were encouraging, a modification of the above procedure was used to obtain more precise data at definite temperatures.

The modified procedure is shown in Figure 2. A glass block approximately 1 inch square and ¼ inch thick was placed in a crucible which was inserted in a larger one. The crucibles and contents were brought to the desired temperature in an electric furnace equipped with automatic temperature control. When this temperature was reached, a small pellet of the volatile salt was dropped into the space between the two crucibles and the outer crucible covered with a loosely-fitting cap. By this arrangement, the vapor of the metallic salt was allowed to react with the glass surface for a period which was fixed at one hour for these experiments. At the end of the test period, the crucibles and glass block were removed and allowed to cool in air.

In order to compare the durability of the surface of a treated sample with that of the untreated glass, recourse

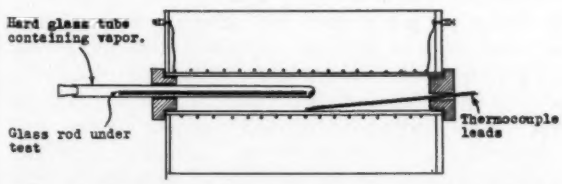


**Fig. 1. Method used in preliminary experiments to determine whether various vapors could be used to improve the durability of glass. A glass rod of poor durability was placed in a tube, containing the desired vapor, which was inserted in an electric furnace with a known temperature gradient. After the test period of one hour, the glass rod was placed in citric acid and the corrosion of the surface observed.**

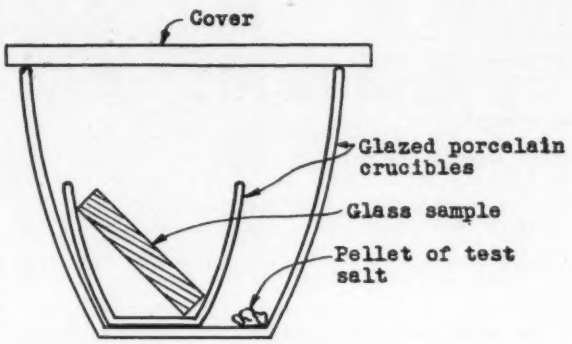


**Fig. 2. Imoroved method of allowing vapor of any desired salt to act on glass sample consisted of placing glass sample in crucible which was inserted in a larger crucible. The temperature was then raised to the desired point, a small pellet of the test salt dropped into the space between the crucibles, and a cover placed over the larger crucible. After the treatment of one hour, the glass sample was tested by the citric acid method.**

was made to the citric acid "spot test" used in the vitreous enameling industry. The glass rod under test was a sodium borosilicate of poor durability, which was coated with a film when subjected to the action of 10 per cent citric acid solution for a period of 10 minutes. The results which are given below therefore refer to these special conditions and additional work would be required before any conclusions could be drawn concerning the application of the method to various other glass compositions.

Using the above testing procedure, the action of various vapors on the glass surface was observed. The vapors tested were those produced by the chlorides of the metals, vanadium, aluminum, cobalt, nickel, manganese, silicon, bismuth, zinc, tin, and iron. The temperatures of testing ranged from 350° to 500° C. The test period was of one hour duration.

Figure 3a is a photograph of the glass specimens after completion of the tests and subsequent acid treatment. Each glass specimen was divided into quadrants and given the treatment depicted in Figure 3b, which shows that half of the sample was rubbed briskly with a cloth after removal from the furnace and before the acid treatment, in order to determine whether the attacked surface could be readily removed. This rubbing treatment affected only the samples heated in the vapors of bismuth and zinc chlorides.

Table I and Figure 3a indicate that the durability of the glass surface was markedly improved by treatment with the vapors of the chlorides of vanadium, aluminum, cobalt, nickel, manganese, and silicon, while no favorable results were noted in the use of bismuth, zinc, tin, and iron chlorides. The cause of the increased resistance of the glass surface to the attack of acid is not known at present. It seems evident that the metal which is present

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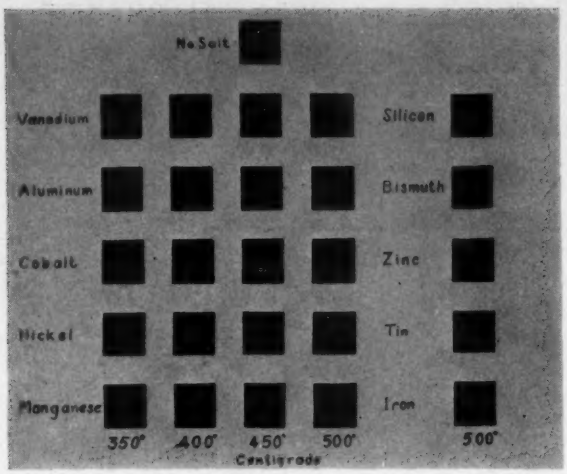
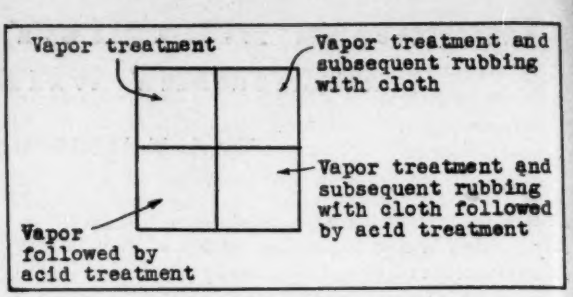




Vapor treatment
Vapor treatment and subsequent rubbing with cloth
Vapor treatment and subsequent rubbing with cloth followed by acid treatment
Vapor followed by acid treatment

**Figs. 3a (left) and 3b. Photograph of glass samples after treatment in the vapors arising from the chlorides of various chemical elements, with subsequent treatment in citric acid. Each sample was divided into four quadrants and given the treatments shown in Fig. 3b. Only the lower halves of the samples shown in Fig 3a were treated with citric acid. A uniformly black appearance of the samples in Fig. 3a indicated that no apparent corrosion of the glass surface occurred. This resistance to attack seemed most pronounced in the case of aluminum chloride.**

in the vapor enters the glass structure and produces a more resisant glass surface. Of the salts tested, it is probable that aluminum chloride would produce satisfactory results at the lowest cost. Additional experiments are being made to apply these results to other glass compositions.

TABLE I

Results of tests of Figure 3a shown in tabular form. Treatment of sodium borosilicate glass in chloride vapors at various temperatures for one-hour period, with subsequent immersion of glass in citric acid (10 per cent solution) for 10 minutes.

| *Vapor acting on glass surface* | *Temperature °C* | *Appearance of glass surface after treatment with citric acid* |
|---|---|---|
| Blank test (in air) | ... | Strongly attacked. |
| Vanadium chloride | 350 | Strongly attacked. |
| Vanadium chloride | 400 | No apparent attack. |
| Vanadium chloride | 450 | No apparent attack. |
| Vanadium chloride | 500 | No apparent attack. |
| Aluminum chloride | 350 | Slightly attacked. |
| Aluminum chloride | 400 | No apparent attack. |
| Aluminum chloride | 450 | No apparent attack. |
| Aluminum chloride | 500 | No apparent attack. |
| Cobalt chloride | 350 | Strongly attacked. |
| Cobalt chloride | 400 | Strongly attacked. |
| Cobalt chloride | 450 | No apparent attack. |
| Cobalt chloride | 500 | No apparent attack. |
| Nickel chloride | 350 | No apparent attack. |
| Nickel chloride | 400 | Strongly attacked. |
| Nickel chloride | 450 | Slightly attacked. |
| Nickel chloride | 500 | No apparent attack. |
| Manganese chloride | 350 | Strongly attacked. |
| Manganese chloride | 400 | Strongly attacked. |
| Manganese chloride | 450 | No apparent attack. |
| Manganese chloride | 500 | No apparent attack. |
| Silicon chloride | 500 | No apparent attack. |
| Bismuth chloride | 500 | Opaque film formed on surface after treatment with vapor. Acid attacked this film. |
| Zinc chloride | 500 | Opaque film formed on surface after treatment with vapor. Acid attacked this film. |
| Tin chloride | 500 | Opaque film formed on surface after treatment with vapor. Acid attacked this film. |
| Iron chloride | 500 | Strongly attacked. |

## CERAMIC ARTS EXHIBIT PROVES HIGHLY SUCCESSFUL

The New York Society of Ceramic Arts held its fortieth annual exhibit during February at the National Arts Club in New York City. As in former years, the entire emphasis was on the craftsmanship of the individual, and this year the emphasis was directed particularly toward *American* craftsmanship. Here the objective was to acquaint both professionals and the general public with the fact that American sources are capable of and actually are producing work of high artistic merit.

In the furtherance of this purpose, world events have created a most favorable situation. They have called a temporary halt to artistic creative effort in many countries of the world and have placed great difficulties in the path of shipping *objets d'art* to this country. This leaves the field wide open to the American artisan to gain merited recognition for his work, and having attained his place in the sun, to hold it securely.

Special efforts to feature glass resulted in some unusually worthwhile exhibits of this medium. Outstanding of these were stained glass by Joep Nicolas and by Rambusch. Here the conventional religious motif received added interest, from the brilliancy of color in one window in particular, and from a technique of silver staining in still another. Rambusch presented a display of glass building block with a decoration painted and fired—a new form of decoration that has just been introduced.

Piero Modigliani's artfibre glass panels introduced a decorative medium entirely new to America and it was so outstanding as to catch the attention of the Metropolitan press. His designs included such varied subjects as snow and marine scenes, religious panels, acquaria, etc. Pastel colors predominated, and one of the most striking effects was produced with simple grey and white.

The WPA glass project in South Jersey contributed a number of hand made objects, though this exhibit did not reflect the degree of skill associated with that undertaking. Verlys showed the designs of Carl Schmitz; Robert May of Duncan and Miller had a very lovely flat dish of opalescent blue. Fostoria showed five pieces of excellent design and quality.

# SULFATES IN GLASS

**By ADDISON B. SCHOLES**

**Fellowship Assistant, Mellon Institute of Industrial Research***

**The current interest in the use of sulfates in glass, and particularly the recent trend toward the use of barium sulfate, has prompted this brief summary of the literature. This review covers the history of the use of sulfates in glass, the action of sulfates in glass, both chemical and physical, and some of the properties of glass, as affected by sulfates.—The Editor.**

Sulfates have been present in the raw materials used in the manufacture of glass, either as impurities or as essential parts, since glass was first made. In commercial glass manufacture, it is virtually impossible to escape the presence of sulfur trioxide in finished glass, either introduced in the form of sulfate impurities in batch raw materials, or formed in the molten glass from the absorption of sulfur dioxide from furnace atmosphere.

The effects of sulfates in the manufacture of glass are, in general, advantageous, because they give decreased melting time, increased fining ability, maintenance of oxygen potential, decreased viscosity at high temperatures, and increased viscosity at low temperatures. Increased refractory attack, likelihood of heterogenity, adverse effect on certain decolorizers, and the necessity for the use of a reducing agent are, however, noticeable when large amounts of sulfate are present in the glass batch.

The analyses of ancient glasses frequently show the presence of rather large amounts of sulfur trioxide, indicating the presence of sulfates in the original raw materials. Ganzenmüller[1], in listing the analyses of ancient Babylon-Assyrian glasses, 1400 B.C., showed $SO_3$ to be present as follows:

| | *Lapis Lazuli* *Per cent* | *Turquoise* *Per cent* |
|---|---|---|
| $SO_3$ content | 1.70 | 1.28 |

Sharp[2], in comparing ancient and modern glass compositions, gave an example of the presence of $SO_3$ to the extent of 1.08 per cent in an Egyptian glass, made about 200 B.C.

There are numerous examples of the presence of sulfates in modern glass batches, and the presence of $SO_3$ in the analyses of finished modern glasses. Biser[3], writing on glass in 1899, lists the following batch for the production of semi-white sheet glass:

| | |
|---|---|
| Sand | 500 |
| Barytes ($BaSO_4$) | 140 |
| Salt cake ($Na_2SO_4$) | 70 |
| Ground Limestone | 160 |
| Charcoal | 10 |
| Cullet | 500 |

An anonymous paper in *Sprechsaal*, 1906[4], gives two batches in which sulfate appears:

| I | |
|---|---|
| Sand | 100 |
| Barytes ($BaSO_4$) | 27 |
| Limestone | 9.5 |
| Glauber's salt ($Na_2SO_4.10H_2O$) | 36 |
| Potassium sulfate ($K_2SO_4$) | 7 |
| Carbon | 4 |
| Cullet | 40 |

| II | |
|---|---|
| Sand | 100 |
| Soda | 30 |
| Barytes ($BaSO_4$) | 13 |
| Saltpetre | 4 |
| Cullet | 30 |
| Manganese | 0.250 |
| Antimony | 0.230 |

Fettke, in 1918[5], lists representative batches, American and foreign, showing the presence of sulfate in the form of salt cake, $Na_2SO_4$, as follows:

| | *American* | *Window Glass* | | | |
|---|---|---|---|---|---|
| | *Bottle Glass* | *Amer.* | *Eng.* | *Fren.* | *Ger.* |
| Sand | 100 | 100 | 100 | 100 | 100 |
| Limestone | 34 | 38 | | 35 | 38 |
| Slaked lime | | | 53 | | |
| Soda ash | | 4 | | | |
| Salt cake | 38 | 40 | 53 | 40 | 45 |
| Carbon | 5 | 8 | 6 | 2 | 3 |
| Arsenic | | 1 | | 1 | |

Sharp[6], in 1940, gives typical analyses of several types of American glass, which show the presence of $SO_3$, and states that the long-accepted sodium sulfate (salt cake) is being replaced by other sulfates, particularly ammonium and barium sulfates.

### Carbon and Sulfate

There are many conflicting reports and views on the action of sulfates in glass. One of the theories on which there is a widespread difference of opinion is the necessity for the presence of a reducing agent in a batch containing sulfate. Several writers refer to the use of reducing agents with sulfates. Taylor[7] suggested the use of sulfur as a reducing agent, to be used with salt cake. Fuwa and Suzuki[8] used ammonium sulfate reduced with an addition of organic matter to produce brown color. Flint[9] proposed the use of a metallic reducing agent. Flint[10] also suggested a method of preparing a batch by ascertaining first the amount of reducing material present as dust, etc., before the incorporation of additional reducing material to complete the sulfate reduction. In contrast Fisher[11], and the Improved Glass Process, Inc.[12] advocated the use of barium sulfate without a reducing agent in the production of crystal glass. Fisher[13] also suggested the reduction of sulfate with sulfide (of barium) in the manufacture of glass. Zhukovskii, Pollyak, and Orlova[14] stated that the addition of coal to sulfate in a glass first adversely effects purification, then improves it. Murgatroyd[15] attributed the reboiling of carbon amber glass to reactions between carbon and undissociated sulfate, with the formation of $SO_2$ and $CO_2$. Krak[16] stated that salt cake cannot be used in lead glasses, since the reducing conditions necessary for the use of salt cake would reduce the lead to metal. He gave the

following reactions, to explain the action of salt cake in melting glass:

$$2Na_2SO_4 + C = 2Na_2SO_3 + CO_2$$
$$Na_2SO_3 + SiO_2 = Na_2SiO_3 + SO_2$$

Dralle[17] and Scholes[18] repeat these equations. Scholes further reported that somewhat less than the amount of carbon theoretically required should be used to avoid reduction of sulfites to sulfides, with resulting amber glass. An anonymous writer[19] also stated that excess carbon in the batch would result in the formation of sulfides, giving a yellow-brown color to the glass. This writer also had found that small quantities of sulfates reduce themselves or react in the absence of carbon. Steinke[20], discussing the factors that affect the fining of mirror glass, was of the opinion that for glasses containing $Na_2SO_4$, the amount of carbon added to the batch should be governed by the furnace atmosphere. McSwiney[21] concluded that in the use of barite, no reducing agent is needed for small amounts. Regarding the use of large amounts of salt cake, Trusov and Rodin[22] found that charcoal must be intimately mixed with the sulfate. Gehlhoff, Kalsing, and Thomas[23] found, in their experiments with sulfates, that when a glass batch contained over 1 per cent salt cake, it was necessary to add carbon. Jebsen-Marwedel[24] stated that with up to 2 per cent salt cake in a soda-lime-silica glass of the composition: $SiO_2$ — 72 per cent; CaO — 14 per cent; $Na_2O$ — 14 per cent; carbon was not needed. Tammann and Oelsen[25], working on reactions in glass melting, gave the following batch and explanation:

| | |
|---|---|
| Sand | 1000 |
| Salt cake | 400 |
| Limestone | 400 |
| Sugar charcoal | 25 |

Sodium sulfate is reduced to sodium sulfide by carbon at 740°C, and the sulfide forms sodium carbonate and calcium sulfide by intereaction with calcium carbonate. The double carbonate of sodium and calcium is formed. This reacts with silica at 600°C to give off carbon dioxide. Sodium sulfate and sodium sulfide react to form the oxide of sodium and sulfur dioxide, which is evolved. Calcium sulfate and calcium sulfide react similarly to form calcium oxide and sulfur dioxide at 850°C. Salt water gall results from insufficient reduction of sodium sulfate. This separation is caused by the presence of silica, but can be eliminated by the addition of fine carbon. The glass should be clean at 1240°C. The reactions were determined by means of heating curves combined with analytical data.

Jebsen-Marwedel and Becker[26] found that from 2.6 per cent to 4.3 per cent salt cake in the batch with from 3.3 per cent to 7.0 per cent of the salt cake weight as carbon gave the best glass for color, fining, absence of gall, and fusion. Salmang and Merten[27], in an investigation on sulfates, found that carbon influences the dissociation of a sulfate. Fettke[5] gave the factor 0.065, which when multiplied by the total salt cake equals the total coal to be added to the batch.

**Melting and Fining**

This subject is also definitely controversial. Jebsen-Marwedel[28] stated that increasing the silica content of a glass tends to displace more $SO_3$, and this displacement of $SO_3$ as the solution of $SiO_2$ progresses is an important factor in fining. The findings of Stanworth and Turner[29] on the effect of sulfates upon melting and fining are: (a) Additions to the glass batch of salt cake up to 5 per cent increase the rate of decomposition of silica from 700°C to 800°C, (b) At 1200°C to 1400°C, the mixture without salt cake melts faster than the mixture with 1 to 5 per cent $Na_2SO_4$, (c) Above 1400°C, each mixture melts approximately the same, (d) The elimination of fine seeds is aided by $Na_2SO_4$, (e) Sulfur trioxide decomposes rapidly at 1400°C, (f) The loss of retained $SO_2$ is slow at temperatures over 1400°C. Noel[30] was of the opinion that the action of $(NH_4)_2SO_4$ is first a mechanical stirring by $NH_3$, given off during the reaction with soda ash. This results in the formation of sodium sulfate, which then undergoes its characteristic decomposition. He then stated that, for these reasons, ammonium sulfate should be a better fining agent than sodium sulfate. His theories were substantiated by experimental data. Among the first exponents of the use of ammonium sulfate in glass, following careful experiments, were Turner and Warren[31], who found that $(NH_4)_2SO_4$ in amounts up to about 10 lbs. per 1000 lbs. of sand was more effective than salt cake, both as an aid to melting, and as a fining agent. These data were later verified by Vickers[32] working on a large scale. Nadel[33] also reported ammonium sulfate had a favorable influence on melting and fining, and advised the use of ammonium nitrate with ammonium sulfate for best results. This school of thought is in contradiction to that which advocates the use of a reducing agent with sulfates. Springer[34] advocated the use of Glauber's salt as a good fining agent in ordinary glass, but found that it produced objectionable foam in high-alumina glasses. He also suggested the use of salt cake and saltpetre to shorten both melting and fining time, and found that other sulfates such as those of aluminum, barium and calcium have certain fining actions. Springer proposed furthermore, that the use of a chloride or nitrate with ammonium sulfate and other ammonium salts helps to shorten melting and fining time.

Preston, Turner, and Laithwaite[35] found that the amount of sulfate volatilized from a glass is approximately proportional to the initial sulfate concentration, and that some $SO_3$ remains in the glass in each case. Volosevich and Zagniborodov[36] experimented successfully in the replacement, with sulfates, of the entire alkali content of a batch. Kitaigorodskii and Tzaritsuin[37] used sodium bisulfate successfully in the manufacture of glass, replacing soda and other sulfates. Motchalov and Chomenko[38] claim that an addition of 5 per cent ammonium sulfate to a batch accelerates fusion time by as much as 30 to 36 per cent. Greater amounts of ammonium sulfate, however, retard fusion. Zak and Iofe[39] state that from 0.5 to 8 per cent of salt cake does not influence the speed of crystallization of window glass in the range of 800°C to 1000°C. Partridge[40] found that the scum on a lead glass was generally alpha cristobalite, and that according to experiments only sulfur dioxide caused its occurrence. Sulfur dioxide in an oxidizing atmosphere also caused the formation of deposits of sodium, potassium, and lead sulfates. Kitaigorodskii[41] observed accelerated melting of glass with the addition of 1 to 2 per cent of ammonium salts. Samsonov[42] concluded that of the ammonium salts, ammonium sulfate had the greatest beneficial influence on melting. He also stated that

the reaction between ammonium sulfate and soda ash had favorable influences, because the ammonia liberated gave accelerated mixing, and displaced air from the batch. He advised against the use of ammonium sulfate in potash glasses, since one of the reaction products is potassium sulfate which dissociates with difficulty. Gelstharp and Parkinson[43] found by experiment, that if the ratio of soda to lime in a glass were less than 2:1, it was necessary to have sodium sulfate present to prevent white scum formation. Rrink[44] states that $Na_2SO_4$ aids melting and fining by reacting with silica at about 1370°C, and that the properties given the glass by sodium sulfate are due to undecomposed sulfate. Potts[45] demonstrated by experiment, that the melting time of a soda-lime-silica glass was reduced by any sulfate, with the first minimum point occurring at about 0.5 per cent of the equivalent of oxide. Weyl and Pincus[46] report that with regard to fining, the more kinds of gas present in a bubble, the lower must be the partial pressure of each single gas. Better fining results, therefore, since the partial pressure of the dissolved gases is high and their removal is facilitated. Also, they state that from the viewpoint of fining, one should be interested in materials which will hold their oxygen up to high temperatures, and make it available during the fining interval, and that good fining agents should react with the excess oxygen present in the form of small seeds.

Jebsen-Marwedel[24] concluded that the ratio between the volume and the free surface of the mixture, the partial pressure of the atmosphere above the mixture, and the total volume of the mixture, affect the rate of disintegration of sulfur trioxide and carbon dioxide. He also is convinced that the evolution of $SO_3$ proceeds more rapidly with increasing sulfate content, due to the increase in reaction surface. He further concludes that about 1 per cent $SO_3$ is retained in the glass, regardless of the original $SO_3$ content. Small quantities of sulfate without carbon, in his opinion have the same melting and fining action as large quantities with carbon, over the same period of time, carbon merely accelerating the early evolution of $SO_3$. Salmang and Becker[47] declared that glasses containing no sulfate can contain oxygen only if materials are present which exist in different states of valency. Bezborodov and Abel'Chuck[48] obtained decreased melting and fining time with ammonium sulfate, and explained this as follows:

above 250°C } $(NH_4)_2SO_4 + Na_2CO_3 = Na_2SO_4 + 2NH_3 + CO_2 + H_2O$
below 400°C } $(NH_4)_2SO_4 + CaCO_3 = CaSO_4 + 2NH_3 + CO_2 + H_2O$

above 400°C $(NH_4)_2SO_4 = 2NH_3 + H_2O + SO_3$

Blyumen[49] described the successful use of barite in place of barium carbonate, with no difficulty in melting or fining. An anonymous writer[50] experimented with sodium sulfate, and noted a rapid reduction in $SO_3$ content during the early stages of melting, while the amount of $SO_3$ remaining in the finished glass seemed to be stabilized unless prolonged heating took place. Zhukovskii, Pollyak, and Orlova[14] listed a number of factors influencing the formation of seeds in an aluminomagnesia glass containing sulfate, among which are:

1. The addition of sodium sulfate at 0.5 per cent $Na_2O$ in the finished glass improves purification.
2. The increase in $SO_2$ in the furnace atmosphere hampers fining.
3. Severe cooling lowers the number of bubbles.
4. Repeated heating of a sulfate glass results in reboiling, the number of bubbles formed being proportional to the sulfate concentration.
5. Increase in $SO_2$ in the furnace atmosphere increases the dissolved $SO_2$ in the glass.

Krak[16] limited the use of sulfate to poor grade glass for the prevention of scum. Scholes[51] stated that excess sulfate, unreduced, rises to the surface of a molten glass bath, and takes undissolved silica scum into solution. He further added that salt cake may be present in as large amounts as one-fifth the soda in high-lime glasses. An anonymous writer[19] held the view that cords may result from "salt-water" gall, if not decomposed, due to the solution of CaO; and that more $SO_3$ is retained in a glass in an oxidizing rather than a reducing atmosphere. McSwiney[21] noted that barite appears to serve well as an aid to melting and fining, and that batch piles, on melting with barite, show vigorous action, much like high-nitre batches. He added that increased brilliance noted with the use of barite is more probably due to more fluid glass at high temperatures, resulting in smoother articles, rather than to the effect of the small amount of resulting BaO in the finished glass. Gehlhoff, Kalsing, and Thomas[23] showed that 0.1 per cent $Na_2SO_4$ gave an increase in total gas bubbles in glass when held at 1400°C, and cooled, while 0.5 per cent gave best fining. Jebsen-Marwedel[24] showed that evolution of bubbles from a sulfate glass was rapid in the first ten minutes of melting, then gradually diminished thereafter. Jebsen-Marwedel, working with Becker[26], demonstrated that a reducing atmosphere resulted in a greater decrease in $SO_3$ content in a glass than an oxidizing atmosphere, for the same series of increasing temperatures. Salmang and Merten[27] found that the $SO_3$ content of a glass was dependent on thermal dissociation with silica, and that the $SO_3$ content of the glass does not affect solubility.

**Refractory Attack**

Ross[52] showed that compounds of sodium under strongly reducing conditions had more effect on the wearing away of tank blocks than under oxidizing conditions, and that salt water (gall) attacks refractories by actual penetration of the blocks, rather than by surface attack. Endell, Fehling, and Kley[53] reported that the lower the viscosity for a given slag or glass, the greater the attack; the higher the temperature, the greater the attack; that the attack by a glass is nearly independent of the glass or block composition, but increases markedly with increasing fluidity of the glass. Schurecht[54] reported that the more fluid a slag or glass, the greater its penetration in a given refractory, and the greater its attack; and that, apparently, the composition of a glass has little to do with its refractory attack. Dietzel[55] showed that sulfate as $Na_2SO_4$ had a great effect on the corrosion of tank blocks, especially if carbon were present. Scholes[56] stated that when a layer of glass gall exists on the surface of a glass, its low viscosity enables it to penetrate the refractories readily, with resulting corrosion. An anonymous writer[19] reported that the active ingredient in block attack is mainly molten sodium sulfate. Trusov and Rodin[22], describing the action of a high-sulfate batch, stated that its use affects refractories severely.

(*Continued on page* 126)

# ADDITIVE FACTORS FOR CALCULATING THE COEFFICIENT OF THERMAL EXPANSION OF GLASS FROM ITS COMPOSITION

By KUAN-HAN SUN and ALEXANDER SILVERMAN*

The additive formula suggested by Winkelmann and Schott[1] is still the most important one in the calculation of coefficient of thermal expansion of a glass from its composition. The formula based on the ideal behavior of the constituents in glass is rather simple:

$$\alpha = p_1\alpha_1 + p_2\alpha_2 + p_3\alpha_3 + \ldots\ldots \quad (1)$$

In the formula, $\alpha$ is the coefficient of linear expansion of glass, $p_1$, $p_2$, $p_3$ . . . the percentages by weight of the component oxides, and $\alpha_1$, $\alpha_2$, $\alpha_3$ . . . their respective factors of the coefficient of linear expansion. The coefficient of linear expansion of a glass, as commonly used in the literature, is the mean value for the range of temperature through which the expansion is approximately a linear function of temperature. If the coefficient of cubical expansion is desired, both sides of formula (1) may be multiplied by 3.

It is our belief that for glasses containing no peculiar constituents such as boric oxide (and alumina within certain limits), the above linear addition formula is approximately true for most of all glass systems and composition ranges.

Recently Badger and White[2] have published thermal expansion data for a series of glasses in which various oxides were introduced into a soda-lime-silica glass of the composition: 72.5 per cent $SiO_2$, 10.1 per cent CaO, and 17.4 per cent $Na_2O$ ($1.4Na_2O.0.09CaO.6.0SiO_2$ in moles). From their data, a series of additive factors for various oxides could be derived by applying the following simple equation:

$$p_A\ \alpha_A + p_B\alpha_B = \alpha \quad (2)$$

or

$$\alpha_A = \frac{\alpha - p_B\alpha_B}{p_A} \quad (3)$$

where $p_A$ and $p_B$ are percentages in weight of the added oxide and the soda-lime-silica base glass, respectively, in the glass, $\delta$ is the measured coefficient of expansion of the glass, and $\delta_A$ and $\delta_B$ are the factors for the coefficient of expansion of the added oxide A, and the base glass B, respectively. The measured mean coefficient of expansion $\alpha_B$ to 300° C. for the base glass is $102\times10^{-7}$ cm./cm./° C. The factors for various oxides thus calculated are listed in Table I.

It is dangerous to establish new factors for various oxides, each of which was derived from only one glass. The purpose of this paper is to compare the factors with that derived by other investigators as compiled in Table II. It is to be noted that some factors derived by Winkelmann and Schott and by Mayer and Havas[3] were obtained also from the data of only one glass. As a matter of fact, most of the well known factors of Mayer and Havas were derived from only two glasses or enamels for each oxide.

We believe Table II is probably the most comprehensive table for the expansion factors ever compiled. It is interesting to see that the value for boric oxide (as derived by various investigators) varied from —6.6 to +5.4. The peculiar behavior of boric oxide has been well known for years. The properties contributed by all other oxides in glass deviate only little from that of the oxides in the pure state, but boric oxide may give abnormal deviation according to the particular system and composition range. In the pure vitreous state, boric oxide has a relatively large linear expansion, namely $1525\times10^{-8}$ [16] (about 30 times larger than that of silica), and its contribution to the expansion of boric oxide-silica glasses does not deviate very much from this value. But if some sodium oxide is introduced into the boric oxide-silica glass then boric oxide will not contribute its own share of expansion and will even reduce the expansion contributed by the other constituents. The so-called negative factor resulted. Biscoe and Warren[17] explain that, in the presence of sodium oxide, boron changes to the more rigid configuration of four coordinations, and the coefficient of expansion is thereby reduced. The soda supplies the extra oxygen needed by boron. Glasses containing high percentages of boric oxide behave normally, showing no more shifting in coordination number.

The factor for alumina calculated by us was also negative. English and Turner[18] also mentioned a negative value for alumina. No data are yet available to show any maxima or minima for alumina in the property-composition curves, as in the case of boric oxide. This, as pointed out by Turner and his associates[19], may require a series of glasses containing very high percentages of alumina, which has not yet been investigated. The senior author has long thought that aluminum may take the place of silicon in glass rather than that of calcium or other cations as is the traditional view. The negative

**TABLE I**

**Factors of Expansion For Various Oxides From Data of Badger and White[2]**

| Glass Number | % Base Glass $p_B$ | Added Oxide A | % Added Oxide $p_A$ | Obs. Mean Coef. of Exp. to 300°C. $\alpha\times10^7$ | Factor of Expansion $\alpha_A\times10^7$ |
|---|---|---|---|---|---|
| 1 | 100.0 | .... | 0 | 102 | .... |
| 5 | 98.7 | $Li_2O$ | 1.3 | 108 | 5.64 |
| 6 | 97.3 | $Na_2O$ | 2.7 | 117 | 3.44* |
| 7 | 95.9 | $K_2O$ | 4.1 | 110 | 2.97 |
| 8 | 96.5 | MgO | 3.5 | 104 | 1.59 |
| 9 | 95.2 | CaO | 4.8 | 103 | 1.23 |
| 10 | 87.9 | BaO | 12.1 | 108 | 1.52 |
| 11 | 93.2 | ZnO | 6.8 | 100 | 0.727 |
| 12 | 96.9 | $B_2O_3$ | 3.1 | 98 | —0.271 |
| 13 | 95.6 | $Al_2O_3$ | 4.4 | 97 | —0.343 |
| 14 | 94.9 | $SiO_2$ | 5.1 | 99 | 0.431 |
| 15 | 83.3 | PbO | 16.7 | 120 | 2.10 |
| 16 | 93.3 | $Fe_2O_3$ | 6.7 | 105 | 1.47 |
| 17 | 93.7 | CoO | 6.3 | 101 | 0.863 |
| 18 | 93.7 | NiO | 6.3 | 103 | 1.18 |
| 19 | 93.4 | $Mn_2O_3$ | 6.6 | 110 | 2.23 |
| 39 | 93.3 | $TiO_2$ | 6.7 | 97 | 0.273 |
| 41 | 92.5 | $V_2O_5$ | 7.5 | 108 | 1.82 |
| 42 | 90.0 | $ZrO_2$ | 10.0 | 93 | 0.120 |
| 43 | 86.6 | $CeO_2$ | 13.4 | 99 | 0.796 |

*This value was derived from glasses 1, 9 and 14 by solving simultaneous equations.

## TABLE II††

**Factors (X10⁶) For Calculating the Coefficient of Linear† Expansion of Glass Based on Winkelmann and Schott's Formula.**

| Oxides | Winkelmann & Schott[1] | Mayer & Havas[2] | English & Turner[4,5] | Mori[6] | Renn[7] | Fetterolf & Parmelee[8] | Hall[9] | Gould & Hampton[10] | Manson[11] | Waterton & Turner[12] | Gilard & Dubrul[13] (a+b.p)‡ | Fuwa[14] | W. B. Silverman[15] | Factors From Badger & White's Data (Table I) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $P_2O_5$ | 6.67 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| $V_2O_5$ | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 18.2 |
| $As_2O_5$ | 6.67 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| $Sb_2O_5$ | ... | 12.0 | ... | ... | ... | ... | ... | ... | 12 | ... | ... | ... | ... | ... |
| $SiO_2$ | 2.67 | ... | 0.5 | 0.5 | 0.5 | 0.5 | ... | 0.5 | 0.5 | 0.5 | 0.4 | 0.5 | 2.8 | 4.31 |
| $TiO_2$ | ... | 13.67 | ... | ... | ... | ... | ... | ... | 13.7 | ... | 2.0 | ... | ... | 2.73 |
| $GeO_2$ | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 5 to 7 | ... | ... | ... |
| $ZrO_2$ | ... | 7.0 | 2.3 | ... | ... | ... | ... | ... | ... | ... | 1.25—0.25p | ... | ... | 1.20 |
| $SnO_2$ | ... | 6.67 | ... | ... | ... | ... | ... | ... | 6.67 | ... | ... | ... | ... | ... |
| $CeO_2$ | ... | 14 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 7.96 |
| $ThO_2$ | ... | 21 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| $B_2O_3$ | 0.333 | ... | —6.6 | ... | 0.333 | ... | 2 | 5.4 | 2 | ... | ? | ... | ... | —2.71 |
| $Al_2O_3$ | 16.67 | ... | 1.4 | 15.3 | 15.0 | ... | 5 | 3.8 | 1.73 | ... | 2.0 | 1.4 | 2.4 | —3.43 |
| $Cr_2O_3$ | ... | 17 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| $Mn_2O_3$ | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 22.3 |
| $Fe_2O_3$ | ... | 13.3 | ... | ... | ... | ... | ... | ... | ... | ... | 1.5+0.2p | 5 | ... | 14.7 |
| $Sb_2O_3$ | ... | ... | ... | ... | ... | ... | ... | 7.0 | ... | ... | ... | ... | ... | ... |
| MnO | ... | 7.33 | ($Fe_2O_3$+FeO) | ... | ... | ... | ... | ... | ... | ... | 7.0+0.15p | ... | ... | ... |
| FeO | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 18 | ... | ... |
| CoO | ... | 14.7 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 8.63 |
| NiO | ... | 13.3 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 11.8 |
| CuO | ... | 7.33 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| BeO | ... | 15 7 | ... | ... | ... | ... | ... | ... | ... | ... | —4 (?) | ... | ... | ... |
| MgO | 0.333 | ... | 4.5 | 4.5 | 4.5 | ... | 2 | 4.5 | 2 | ... | 0 | ... | ... | 15.9 |
| CaO | 16.67 | ... | 16.3 | 15.3 | 16.3 | ... | 15 | 16.3 | 15 | 16 | 7.5+0.35p | 16.3 | 13.6 | 12.3 |
| ZnO | 6 | ... | 7.0 | ... | 6 | 6.17 | 10 | 9.8 | 6 | ... | 7.75—0.125p | ... | ... | 7.27 |
| BaO | 10 | ... | 14.0 | ... | 10 | 19 | 12 | 11.7 | 17.3 | ... | 9.1+0.14p | ... | ... | 15.2 |
| PbO | 10 | 14 | 10.6 | 9.38 | 10 | ... | 7.5 | ... | 14 | ... | 11.5—0.05p | ... | ... | 21.0 |
| $Li_2O$ | 6.67 | ... | ... | ... | ... | ... | ... | ... | ... | 49 | 59.5—0.5p | 66.7 | ... | 56.4 |
| $Na_2O$ | 33.3 | ... | 43.2 | 47 | 43 | 41.7 | 38 | 43.2 | 41.7 | 41.8 | 51.0—⅓p | 50 | 38.4 | 34.4 |
| $K_2O$ | 28.3 | ... | 39.0 | ... | 40 | ... | 30 | 34.2 | 30 | 34 | 42.0—⅓p | 39 | ... | 29.7 |
| $Rb_2O$ | ... | ... | ... | ... | ... | ... | ... | ... | ... | 26 | 28.0—0.25p | ... | ... | ... |
| NaF | ... | 24.7 | ... | ... | ... | ... | ... | ... | 24.7 | ... | ... | ... | ... | ... |
| $CaF_2$ | ... | 8.33 | ... | ... | ... | ... | ... | ... | 8.33 | ... | ... | ... | ... | ... |
| $AlF_3$ | ... | 14.7 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| $Na_3AlF_6$ | ... | 24.7 | ... | ... | ... | ... | ... | ... | 24.7 | ... | ... | ... | ... | ... |

† In order to obtain cubical factors, the linear factors are multipled by 3.
‡ p = % oxide, and $\alpha = \Sigma$ (a + b.p.) . p.

value for alumina may serve as further evidence for our view.

As seen from Table II, the alkalis contribute greatly to the expansion of the glass, and their factors of expansion vary inversely as the molecular weights. Silica contributes least to the expansion of glass.

The divergences of the factors derived by the various investigators may be attributed to the following reasons:

A. The coefficient of expansion is a function of temperature. The relationship between the expansion and temperature for a certain glass is approximately linear below the critical temperature and a mean value can be derived. However, this mean value varies with the ranges of temperature adopted. The ranges of temperature adopted by different investigators are usually not identical.

B. In no sense is glass an ideal solution. We would naturally expect the factors to be a function of compositions. The factors in Table II were usually derived from various kinds and compositions of glasses, and their values may differ.

C. Many factors in Table II were derived from glasses containing boric oxide. As indicated above, this oxide shows abnormal behavior which affects the factors of other oxides. Except for specific systems, we suggest that no definite factor should be assigned to boric oxide, and those factors derived from glasses containing boric oxide should be used with extreme care.

D. Some of the factors were derived primarily from enamels, which contain crystalline phases. The expansion values derived from such non-homogeneous systems will be different.

E. The errors in measurement should not be overlooked. The expansion of glass may vary with methods of measurement, with investigators in different laboratories, and with the annealing conditions of the glass.

Many people have used Winkelmann and Schott's formula for the calculation of expansion from composition, but there is a fundamental error in the formula. From the definition of the coefficient of cubical expansion:

$$3\alpha = \frac{1}{V}\frac{dV}{dt}$$

where V and t are the volume and temperature respectively, it is easy to see that instead of using weight percentages in Winkelmann and Schott's formula, the volume percentages should be adopted. In other words, even though each constituent in glass behaves ideally, Winkelmann and Schott's formula will fail to show the linear additivity of the expansion. However, there is a difficulty in using volume percentages, as we do not know, in most of the cases, the true volume contributed by each individual constituent. (*Continued on page* 125)

# LAMINATING "HI-TEST" SAFETY GLASS AT L-O-F

The vinyl resin plastic used in the manufacture of Hi-Test safety plate glass is a synthetic resin furnished to the Libbey-Owens-Ford Glass Co. by several manufacturers. It is delivered in ribbon form, fifteen one-thousandths of an inch thick, and dusted with soda so it will not stick together when wound in rolls. Even after the soda is washed off the plastic appears opaque, but it changes to the transparent state when subjected to heat and pressure in the autoclaves, as described later.

The first step in the preparation of the plastic to become the middle of a safety-glass sandwich, is to pass the ribbon through a "seasoning" oven, this operation having the two-fold objective of drying the plastic and normalizing it from a shrinkage standpoint. The plastic must have a very low moisture content to prevent separation of the glass from the plastic and to forestall bubbling if the finished product is subjected to a high temperature. After seasoning the plastic is festooned on trays and kept on shelves until the material reaches room temperature.

**The vinyl resin plastic used in the manufacture of Libbey-Owens-Ford Hi-Test safety glass is tough and stretchy. Pieces of plastic to fit into window lights for automobiles are cut from a ribbon of plastic, 0.015 in. thick, and piled ready for further operations.**

From this point in the process until the plastic has passed through an autoclave, great care is taken to preserve the low moisture content achieved in the seasoning oven. The storage cutting and assembly rooms are all air-conditioned, the temperature being maintained between 65 and 70 deg. F., with a relative humidity of not more than 20 per cent.

### Cutting the Plastic

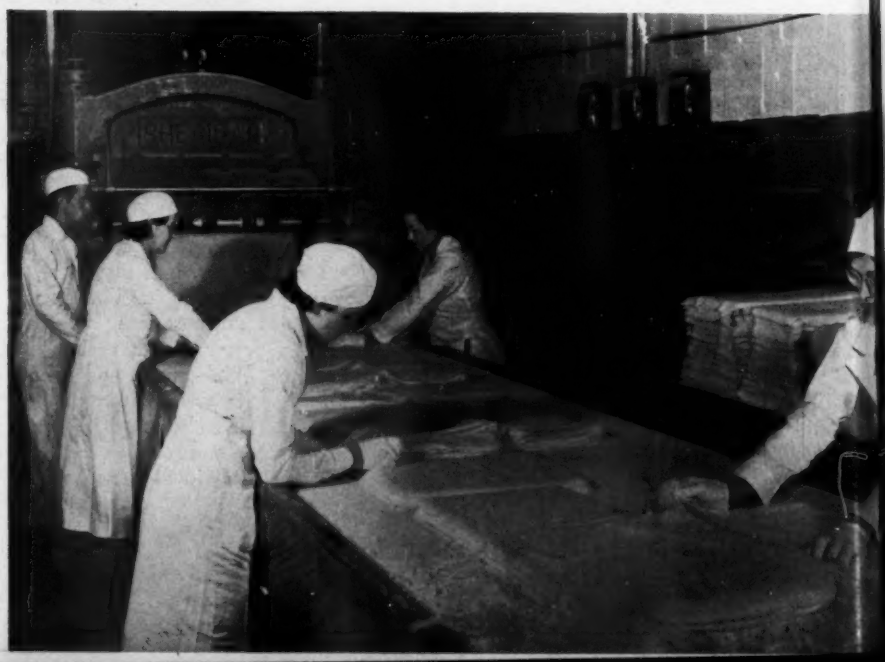
The next operation is to run the plastic ribbon through a continuous-feed cutting press which cuts the material into the various shapes needed for windshields, door lights and other automobile windows. The plastic is very elastic and care must be taken in the cutting operation to prevent stretching and insure full size pieces of plastic for the assembly.

Before assembly with the glass sheets of the sandwich, the soda is removed from the sheets of plastic by running them through high-pressure sprays of warm water, after which the sheets are immediately sprayed with cold water to stiffen them for passage through the drying rolls. Finally, high-velocity air is blown over the plastic sheets to remove any last traces of moisture. It can be readily understood that the washing operation to remove the soda mus be done quickly, since such elaborate precautions have already been made to protect the material from moisture.

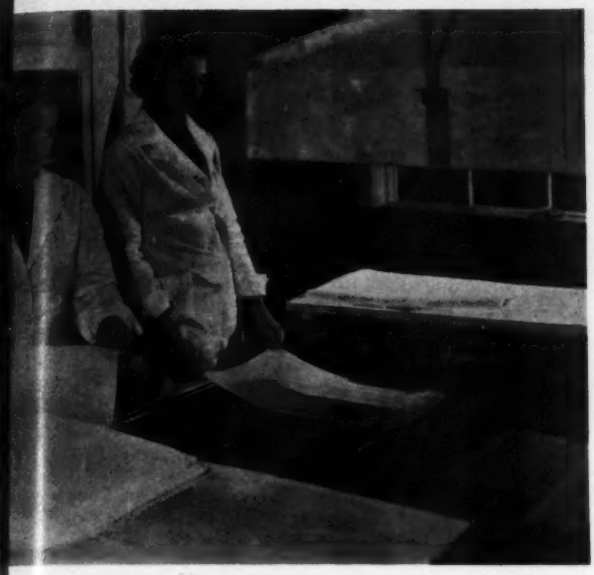
As the plastic comes off the washing machines it is inspected for dirt and other defects, the inspection method utilizing polarized light. The polarized light inspection method was perfected in the L-O-F plant and has aided materially in locating and reducing certain types of defects which were formerly very difficult to see. Many rejects that were formerly blamed on the presence of soda due to improper washing have been found to result from other causes. After inspection the pieces of plastic are ready for assembly with the mating pieces of glass.

### Glass Preparation

The ground and polished plate glass used in Hi-Test safety glass is cut to pattern on semi-automatic machines,



**Cutting of the plastic is performed by a continuous-feed cutting machine into which the ribbon is carefully fed to prevent stretching. These operators are sorting and piling the cut pieces of plastic.**



**Before assembly with the glass, the pieces of plastic are passed through a washing machine to remove the bicarbonate of soda with which the plastic ribbon was originally covered to prevent sticking in the roll.**

in which a carriage riding on a strip of metal shaped to the pattern, trails a small steel cutting wheel. It is, of course, important that the lights be cut exactly to pattern so that they may be assembled accurately and, after edging, will fit snugly into the window channels of the automobile for which they are made.

After cutting, the glass is subjected to a washing operation in which it runs through a cleansing solution, is scrubbed with rubber brushes, rinsed in distilled water, and finally dried. The lights pass along the washing-machine conveyor in pairs and after washing are carefully inspected to insure uniform quality. The conveyor then carries the glass through a cooling cabinet and, as they emerge, the lights of glass are ready to meet the prepared sheets of plastic.

In the assembling operation girls place a piece of plastic on one of the lights of the pair and turn the other light over on top of the plastic. Here the glass-cooling operation has its effect, since with cold glass it is possible to slide one light around until it is matched perfectly with the other. The assembled unit now goes through a nipping roll which drives out all the air between the glass and the plastic, and then passes on into a lehr. The roll pressure and the heat from the lehr constitute a prepressing operation which seals the plastic to the glass around the perimeter, this sealing being necessary to prevent penetration of oil when the lights are finally submerged in the autoclave.

The autoclaves are heavy metal vats, filled with oil and furnished with tightly fitting lids that can be clamped shut against pressure. The assembled lights coming off the end of the conveyor line are stacked vertically in tubs, with a piece of corrugated metal separating each light from the adjacent one. Four of these tubs stacked together compose a "shot" for the autoclave and are lowered into the oil by means of a crane, the oil passing through the false bottoms of the tubs and completely submerging the lights.

After the lid is closed the oil is subjected to pressure and, of course, transmits the pressure to the lights, squeezing the glass tightly against the plastic. The oil is also pumped through a heater for about five minutes and is held at a high temperature for about seven minutes. At the end of the desired period, the oil is passed through a cooler until its temperature is down to 165 deg. F., at which point the pressure is released, the lid is opened and the tubs are lifted out. Under this combination of heat and pressure the plastic becomes transparent and is thoroughly bonded to the glass.

Final operations on Hi-Test safety glass are performed in the edging department and include seaming and pencil polishing. Seaming bevels off the rough edges of a light. Pencil polishing forms a symmetrical curve on the edge and gives a smooth polished appearance, such as is needed on the top of a door light or when a light is required to slide in a felt or rubber channel. The trademark is now sandblasted on the safety glass, after which the lights are again washed, inspected, checked on templates for size, and packed ready for shipment.

**Plate glass window lights come from the cooling cabinet on a conveyor in pairs. In the assembly operation the operators place a piece of plastic on one light and turn the other light over on top of the plastic. The sandwich is then prepressed and finally subjected to heat and pressure in an autoclave.**

# INVENTIONS AND INVENTORS

**A Summary of United States Patents of Interest to the Glass Industry Issued during January**

### Compositions

Selenium, used as a decolorizing agent in soda-lime glasses, boils at 688° C and undergoes considerable loss due to volatilization. A. K. Lyle of Hartford-Empire Co. has found that lead selenide is equally satisfactory for decolorizing and that due to low volatility it has practical advantages. It can also be used in substitution for selenium in producing ruby red glass (2,229,-416).

Improved ruby and opal glass of high lustre is claimed by Frank J. Dobrovolny of Niagara Falls to be produced by sodium oxide or other alkali metal oxides replacing soda ash (2,230,199; E. I. du Pont de Nemours & Co.). Quicker melting time, besides the resultant fuel savings, should decrease the loss of volatile constituents such as fluorides and selenides.

For those composite parts of electric discharge vessels which require the fusion of glass to a ceramic material, patent 2,227,770 suggests a lead glass and a spinal ceramic. The latter would be an $MgO—Al_2O_3—SiO_2$ body. The inventor is Alfred Ungewiss, Berlin-Grunewald, Germany, of Steatit-Magnesia Aktiengesellschaft.

### Furnaces

John L. Drake of Toledo provides in patent 2,228,347 (Libbey-Owens-Ford Glass Co.) a regenerative cooling system in the refining end of a glass tank. The purpose is to reduce the glass to a proper working temperature for a sheet or plate glass forming machine. As shown in Fig. 1, checker chambers are arranged on both sides of the furnace, so that cooling air drawn into the system from the atmosphere is heated sufficiently to avoid excessively chilling the glass. To confine the refining zone so that the cooling will not affect glass in the melting end of the tank, it is suggested that a curtain or partition wall

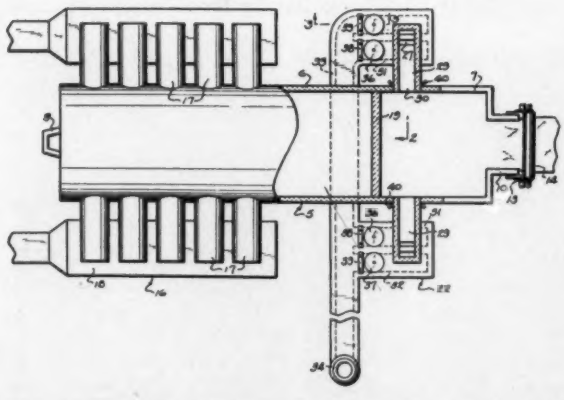


**Fig. 1. 2,228,347: Drake. A tank for supplying molten glass to a sheet forming machine, in which the refining end is separated from the remainder of the furnace by a curtain wall 19 which almost reaches the glass. The glass in the refining end is then chilled to proper working temperature by atmospheric air heated by checkers to a suitable temperature.**

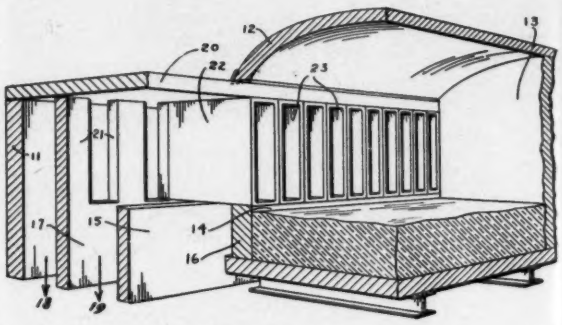


**Fig. 2. 2,228,395: McCauley. In a narrow tank furnace of abbreviated form, the entire sidewall is made up of alternating air and gas flues. The flues are made of hollow tiles of two lengths. The shorter ones terminate at wall 17 and lead to the gas flue 19, while longer tiles extend entirely to the back-wall and connect with the air flue 18.**

be lowered through the cap (19 in Fig. 1) to glass level.

Fig. 2 shows George V. McCauley's design for a glass melting furnace whose entire sidewalls are made up of alternating air and gas flues. This is patent 2,228,395, assigned to Corning Glass Works.

### Feeding, Forming and Shaping

Considerable novelty, in the pressing of half sections of glass blocks on an Owens type bottle forming machine, is revealed in Leonard D. Soubier's patent 2,228,-613 (Owens-Illinois Glass Co.). Only a portion of the mold assembly is shown in Fig. 3. The glass is drawn into a measuring mold which then cooperates with a body mold to give the final shape.

A machine for producing a lip on the ends of glass tubes was patented by Robert H. Koenig, Haddon Heights, N. J. (2,228,010; Kimble Glass Co.). The end of the tube is heated to plastic condition and the tube is rotated fast enough to form the lip centrifugally. Exact shaping of the lip is assured by the action of gauging elements.

To seal ampoules, in which pharmaceuticals are packaged, automatic machines intermittently heat the neck and then constrict it at a drawing station. To avoid the occasional development of complete seals Frank C. Chase of Brooklyn, (2,230,075; E. R. Squibb & Sons), has patented an attachment which inserts a needle into the ampoule while it is being constricted. The needle is cooled while it is in a retracted position.

Glass bulbs for automatic elements and other units wherein liquids are sealed are difficult to close because the heat applied to the end to be sealed, may cause an expansion of the liquid into this region. A. J. Loepsinger, Providence, N. J., in patent 2,227,757 assigned to General Fire Extinguisher Co., forms an initial seal while all but the neck of a charged bulb is immersed in a cooling liquid held at atmospheric temperature, and then obtains a final deep seal by continued heating of the neck, while cooling the bulb and the charge to a lower temperature,

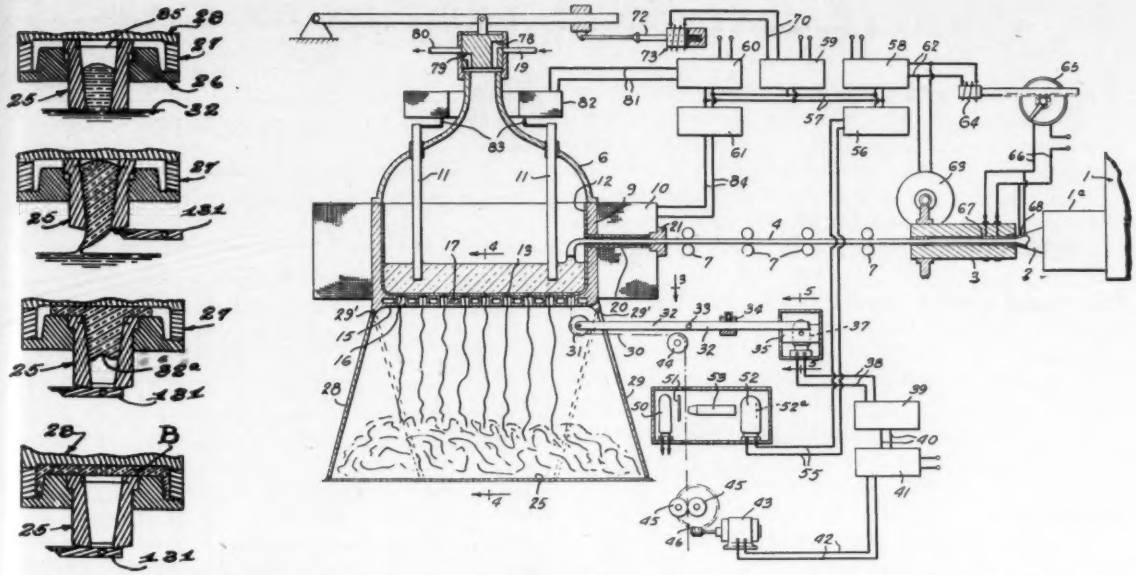


**Fig. 3. (left) 2,228,613: Soubier. In making halves of hollow blocks on an Owens machine glass rises into the measuring mold 25 until the vacuum slot 85 is covered. The charge is severed by knife 131; the measuring mold moves downward allowing the charge to be drawn by vacuum into the body mold where it is given final shaping. Fig. 4. 2,229,489: Barnard. Control of fiber size is obtained by passing a single strand through a photo-electric assembly 50-51-53 in which the degree of light interruption due to fiber diameter actuates apparatus to vary furnace pressure and temperature.**

so as to draw molten glass into the neck by suction caused by contraction of the charge.

### Miscellaneous Processes

Frederick Shurley, Windsor, Ontario, obtained a patent on an automatic machine for loading lehrs with bottles or other glassware. This patent, 2,229,348, and two patents for decorating machines (2,229,346 and 2,229,347), also granted to Mr. Shurley, were assigned to Guthrie Ceramic Labeling & Machinery Co., Inc., Dover, Del. The first of these covers a multicolor printing machine adaptable to glass or other material in the form of sheets. The latter patent concerns a device applicable to the decoration of bottles, and provides an electric control means by which they are successively registered and held momentarily stationary while color is being applied.

A guide rail for guiding articles along a conveyor was patented by H. H. Snyder, A. W. Secoy and J. H. McFee of Lancaster, Ohio. This is patent 2,229,605 assigned to Anchor-Hocking Glass Corp.

The group of patents for glass-to-metal seals issued in January was abnormally large. The process outlined by John J. Hopfield, Toledo, in patent 2,228,352 (Libbey-Owens-Ford), is applicable for sealing metallized glass sheets to metal supports. The metallized sheet is the somewhat familiar product onto which a copper alloy has been sprayed with a metallizing gun. To prepare this surface for soldering to a metal element, a flux comprising triethanolamine and a water soluble glycol is applied. Suitable glycols are ethylene glycol, tetraethylene glycol and others. A method for applying glass shields to tubular metal electrodes was described in patent 2,229,329 granted to Frank Kasper, Cicero, Ill., of General Scientific Corp. Patent 2.227,511 to Frederick Reynolds, Newcastle-on-Tyne, England (Thermal Syndicate, Ltd.) concerns a pressure-tight seal between thin metal parts and quartz glass. A technique for protecting a metal-to-glass seal while welding a metal sleeve to an electrode supporting rod is described in patent 2,229,734 issued to Lynn C. Goodale, Newark, N. J. (Federal Telegraph Co.).

### Plate and Sheet Glass

Laminated glass sandwiching a layer consisting of an acetal of a polymerization product containing free hydroxyl groups and free carboxylic acid groups was patented by Adolf Weihe and Arthur Voss, Frankfort-on-the-Main-Hochst, Germany. This is patent 2,229,781 assigned to General Analine & Film Corp., New York.

A sheet handling device especially adapted for lifting a number of sheets or plates and placing them in proper position upon a horizontal roller runway leading to an edge grinding machine was patented by A. R. Brotherson of Toledo, Ohio (2,228,298, Libbey-Owens-Ford Glass Co.).

### Glass Wool and Fiber

The highly novel apparatus of Fig. 4 for preparing glass wool was covered in patent 2,229,489, issued to Randolph H. Barnard, Toledo, Ohio. A glass strip formed in a separate furnace is conveyed to a closed chamber where it is melted by heat from electrodes 11. Pressure applied to the glass surface forces the glass through tiny apertures to form fibers. An interesting control feature consists in diverting a single fiber over rollers 31 and 44 and through a photo-electric unit. The latter gauges the cross section of the glass strand and then activates control devices which vary the temperature and pressure in the melting chamber. By these means the fiber diameter is controlled.

# CURRENT STATISTICAL POSITION OF GLASS

The glass industry experienced its most active January in history with new records reported for practically every branch of the industry; employment and payrolls were also at peak level for this period of the year. According to THE GLASS INDUSTRY's Production Index, January's output totalled $34,000,000 as compared to $30,000,000 in January 1940.

**Plate glass** produced during January totalled 19,350,059 square feet according to the Plate Glass Manufacturers of America. This was the greatest January volume in the history of the industry, having increased 12 per cent over last year's comparable month. Compared with December 1940 this output represented a contra-seasonal gain of 11 per cent.

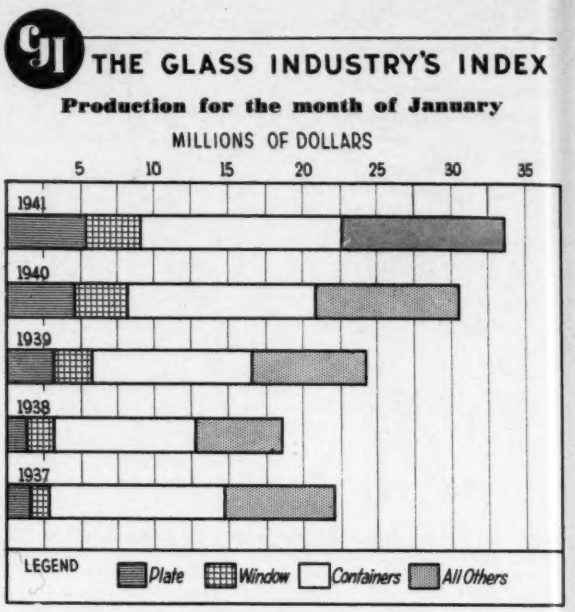
**Window glass** output during January amounted to 1,561,199 boxes, which was 10 per cent greater than last year's comparable month, setting a new monthly record for this industry. This also represented a contra-seasonal increase of 7 per cent over the December volume. Window glass plants operated at 96.2 per cent of capacity in January which was higher than any previous monthly rate on record.

**Glass container** production and shipments were at new January highs also according to the Glass Container Association of America. Production totalled 4,513,900 gross which represented an increase of 7 per cent over December and was 6 per cent above the January 1940 level. Production of all types, with the exception of beer bottles, was greater than last year's volume, with largest gains reported for food containers, pressure and non-pressure ware and milk bottles. Production increases over January a year ago, by classes of ware amounted to: Pressure and Non-Pressure, 28.92; Milk, 23.63; All Other, 10.82; Food, 10.41; General Purpose, 6.56; Fruits and Jellies, 5.22; Liquor, 2.06; Medicine and Toilet, 1.23; Beer, 10.12 (decrease).

Shipments amounted to 4,178,300 gross—an increase of 18 per cent over December and 12 per cent larger than the January 1940 total. Expansion over last year's business was noted in all lines—particularly pressure and non-pressure ware and food containers. Shipment increases over January a year ago, by classes of ware: Fruits and Jellies, 169.72; Pressure and Non-Pressure, 57.06; Food, 19.20; General Purpose, 14.54; Milk, 14.18; Beer, 12.54; All Other, 10.23; Liquor, 4.74; Medicine and Toilet, 3.95.

Stocks on hand at the close of January totalled 10,108,700 gross—7 per cent more than the December figure and 5 per cent above the 1940 level.

During January the glass container industry operated at 65 per cent of capacity.




**Miscellaneous glass products** manufactured during January had a value of approximately $11,000,000. This represented an increase of 30 per cent over last year's comparable figure due to contra-seasonally large volumes in tableware, industrial and technical glassware and other types of pressed and blown glassware. According to a preliminary report of the Bureau of Census, 13

## CURRENT GLASS CONTAINER STATISTICS

(ALL FIGURES ARE IN GROSS)

| | Production | | Shipments | | End of Month Stocks | |
|---|---|---|---|---|---|---|
| *Types of Ware* | *January, '41* | *January, '40* | *January, '41* | *January, '40* | *January, '41* | *January, '40* |
| Food Containers (Narrow neck, wide mouth and pressed) | 1,100,533 | 996,778 | 1,190,568 | 998,806 | 2,098,014 | 2,030,797 |
| Pressure and non-pressure ware | 350,980 | 272,239 | 224,148 | 142,719 | 906,620 | 769,489 |
| Beer Bottles | 294,579 | 327,735 | 140,323 | 124,692 | 722,428 | 791,022 |
| Liquor Ware | 614,269 | 601,857 | 588,744 | 562,104 | 1,742,786 | 1,616,287 |
| Medicinal and Toilet Ware | 1,548,414 | 1,529,504 | 1,467,829 | 1,412,112 | 3,154,515 | 2,971,552 |
| General Purpose Ware | 342,278 | 321,212 | 337,196 | 294,380 | 665,976 | 508,037 |
| Milk Bottles | 206,654 | 167,159 | 205,680 | 180,137 | 299,741 | 290,243 |
| Domestic Fruit Jars and Jelly Glasses | 40,437 | 38,430 | 8,909 | 3,303 | 482,591 | 585,592 |
| All Others | 15,881 | 14,330 | 14,902 | 13,519 | 36,009 | 37,531 |
| Industry Total | 4,513,925 | 4,269,244 | 4,178,299 | 3,731,772 | 10,108,680 | 9,600,550 |

firms manufacturing illuminating ware reported January sales totalling $788,000, which was 4 per cent less than their December business but was 16 per cent above last year's level.

**Employment and Payrolls:** Approximately 80,300 persons were employed in the glass industry during January as compared to 81,500 in December and 74,100 in January of last year.

Glass manufacturers paid out about $9,700,000 in wages during January. This compares favorably with the January 1940 total of $8,400,000.

Machine made tumbler production during January totalled 3,200,229 dozens which was 13 per cent less than last year's comparable figure. The same trend was noted in shipments which declined 11 per cent to 2,641,-145 dozens. During the 12 months ending January 31, 1941, shipments totalled 41,821,759 dozens—an increase of 7 per cent over the previous period. Stocks on hand at the close of January amounted to 8,775,357 dozens which was 12 per cent more than in 1940.

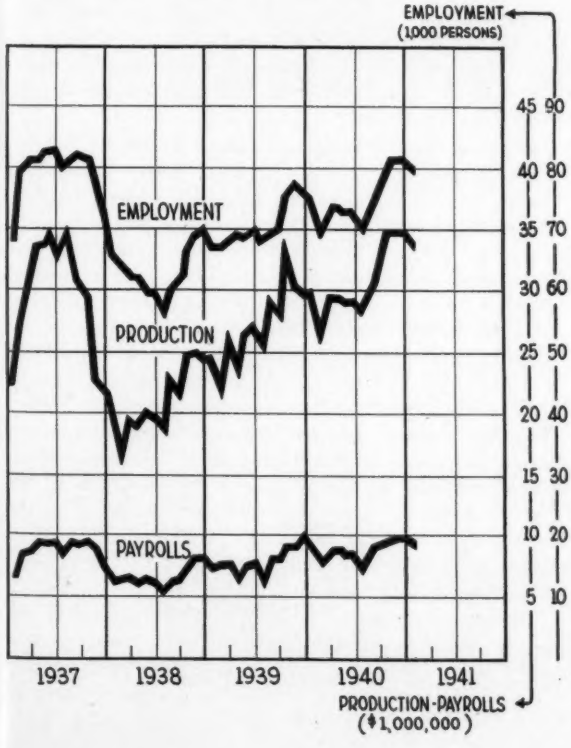
Manufacturer's sales of machine-made table, kitchen and household glassware during January dropped 17 per cent below last year's level to 2,315,866 dozens. During the 12 months ending January 31, 1940 this volume amounted to 33,129,987 dozens.

**Foreign Trade:** Exports of glass and glass products during January increased 3 per cent over the December total recording a value of $1,581,603. This record January volume indicates that the glass export trade will attain even higher levels in 1941; these latest figures place it more than 50 per cent above the January 1940 total. All types of ware, with the exception of plate glass, showed gains over last year. Largest increases were noted in window glass, containers, tableware and miscellaneous pressed and blown glassware items.

Imports dropped 8 per cent from the December total to a new monthly low of $105,572. This was 55 per cent less than 1940's comparable figure.

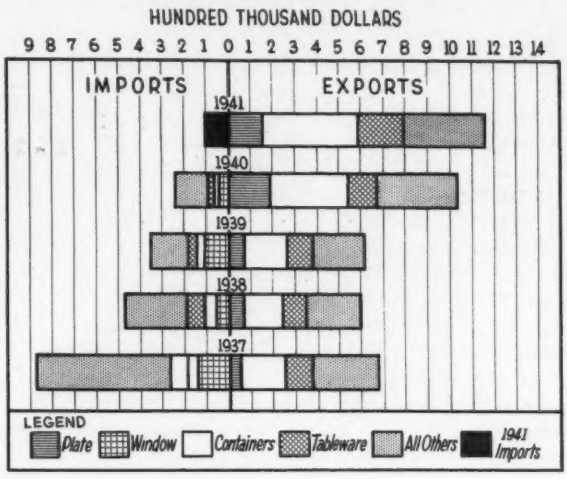
## THE GLASS INDUSTRY'S INDEX

**Monthly Trends Through January, 1941**




## THE GLASS INDUSTRY'S INDEX

**Foreign Trade for January**




FOREIGN TRADE STATISTICS

(VALUES IN $1,000)

| *Exports* | *Jan.* 1941 | *Dec.* 1940 | *Jan.* 1940 |
|---|---|---|---|
| Plate | 150 | 129 | 196 |
| Window | 168 | 133 | 12 |
| Containers | 425 | 375 | 337 |
| Tableware | 190 | 240 | 126 |
| Illuminating ware | 98 | 65 | 74 |
| All other | 551 | 590 | 290 |
| Total | 1582 | 1532 | 1035 |
| *Imports* | | | |
| Total | 106 | 114 | 235 |

• Contracts granting wage increases, one week's vacation with pay, check-off of union dues and to pay time-and-a-half for work done on five holidays, were signed February 15 by representatives of four glass companies after negotiations in Atlantic City with spokesmen for the Glass Workers Union. The agreement ended threat of a strike by 5000 workers of the Federation of Glass, Ceramic and Silica Sand Workers (C. I. O.). The new agreement provided a flat increase of 3 cents an hour for workmen engaged in "continuous process" production, and 2 cents to those doing non-continuous work.

• A new 100-watt fluorescent lamp, the largest yet made and possessing over twice the power of any fluorescent lamp heretofore manufactured for commercial and industrial purposes, was announced recently by the Mazda lamp manufacturers. Five feet long and 2⅛ inches in diameter, it will be available in the 3500K white color.

# STAINED GLASS: ITS BACKGROUND AND FOREGROUND

By HAROLD W. RAMBUSCH*

I should like to consider for a moment that glass which the ceramist and the stained glass craft have in common. Not all ceramics are glazed, but when they are, the glaze in fact and in name is glass. We use the glass differently. Ours is thicker than that of the ceramist. In our case glass is the essential material, in your case it is a finish. But fundamentally the difference is one of light, light in its use and application.

From a matt glazed surface the light is reflected directly. Some glossy surfaces reflect the light directly while many permit the light to penetrate to undercoatings before returning enriched in color and value. When this is the case the ceramic glass and the stained glass partake of a similar nature.

In both, light is the active principle. Ceramics live by reflected light. The purpose of stained glass, however, is to be a source of light; light divided and separated into its component colors; light filtered and bent to reveal its fullest glory; light as a positive element animating the interior, without which nothing has visual existence.

In the Middle Ages the potentialities of glass were fully recognized and quite as fully taken advantage of. The Church being the center of civilization and interest, it was here that the colored glass window had its greatest opportunity. The first good examples date from the Twelfth Century. In the Thirteenth Century it reaches its greatest glory. From then on, sad to relate, it can be broadly said that as the craftsmen became more clever the windows lost in merit. In the thirteenth century color and pattern of light were the dominating interests. As time went on ornament, then story, and finally naturalism preempted the reign of pure color.

The early windows contained only the colored glasses, with faces, hands, drapery and ornaments done in black lines. These are known as "trace lines," and are fired into the glass much the same as it is done with tile. H-shaped lead strips are still used to join the pieces. Later, they learned to use their paint thinner over some areas, and it became shading. These were our early windows—true mosaics of colored light.

I venture to say with some fear of contradiction that we have no proper name for such windows. It is all called stained glass in spite of the fact that "glass stain" was not discovered until the early Fourteenth Century. It was then found that silver salts properly prepared and applied to light tones of glass and fired to the fusing point produced a range of yellows from lemon to deep brown or orange. And now we call it all stained glass. This so called silver stain is absolutely permanent.

The colored enamels which were the next development soon proved to be short of life. Until the advent of enamel each color represented a separate piece of glass. Enamels were an effort to add detail and color without the necessity of cutting the glass and adding a lead line. Enamel did not improve the basic beauty of the window. It did, however, damage the reputation of the craft for permanency.

*From a talk given before the New York Society of Ceramic Arts, February 7, 1941.

In the middle of the last century America produced a great artist, John LaFarge. He produced some truly fine windows in a new type of glass called opalescent. The glass itself was somewhat opaque, hence its name. It varied in thickness, presenting an appearance of modeling. Time proved that LaFarge had produced his results in spite of the medium, for Tiffany and others soon demonstrated opalescent glass to be a complete failure in any hands other than LaFarge's. So opalescent went the way of the glass enamels.

In 1939 the Stained Glass Association of America met in convention in Boston. Charles Connick, who has done so nobly for American stained glass, was then President of the Association and had arranged to have the convention addressed by the two greatest critics and promoters of stained glass in America. What these men said may possibly prove to be as prophetic as it was provocative. Mr. Cram spoke the first day while Mr. Maginnis was still in the West, so neither knew of the other's remarks; still both said essentially the same thing.

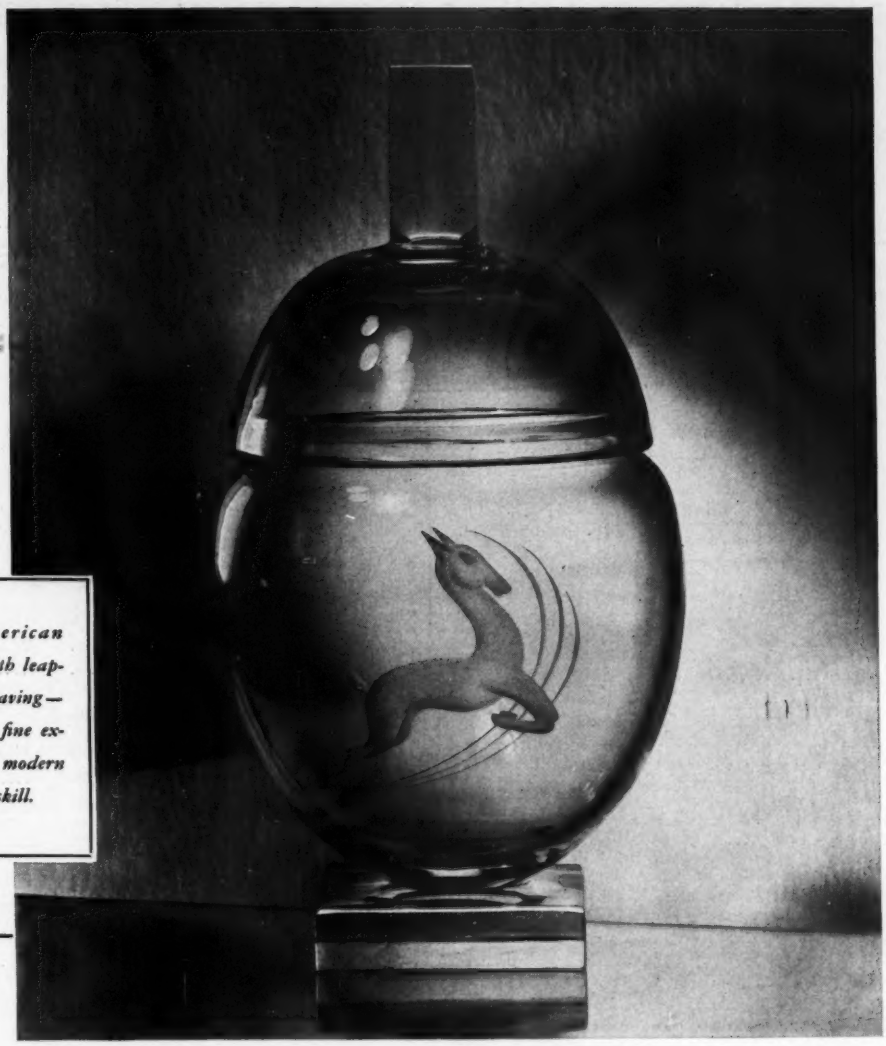
Ralph Adams Cram, being of a philosophical turn of mind, said that he felt that the stained glass craft was susceptible of a new orientation without losing its old values of color and pattern. He suggested that the craft "preserve its substance and alter its accidents" to conform to the pattern of the time. The next day Charles D. Maginnis arrived in Boston, and during the course of a brilliant talk asked "What is this craft doing to meet the impact of modernity?".

These two warnings by the best friends of stained glass have not passed unheeded. The Association has started competitions and offers prizes through the Beaux Arts Institute to the men still at school, for here the change must originate. In the meantime, some tangible works have been produced which at least give promise of new vitality for the craft.

The first example which I consider worthy of mention is the Mapparium in the Christian Science Publishing Society in Boston. Here, the Architect, Chester Lindsay Churchill, conceived the idea of constructing within the building a 30 ft. sphere of bronze and glass which was to be illuminated from without and seen from within. Large sections of glass were made and bent to form in England. American crafts developed a palette of 15 bright colors which appeared harmonious in various juxtapositions. Glass enamels are particularly unruly. They refuse to associate and appear agreeable together. They are brilliant and exciting, much like fluorescent light tubes. The problem of getting 15 colors which would complement each other was, therefore, one of the greatest hurdles. These enamels were fired on to the glass and the sections assembled in Boston. The effect of being on a glass bridge in the center of a colored sphere is truly extraordinary.

The second example I would like to tell you of is less spectacular but probably susceptible of more general application. With our modern casement windows and the general simplicity of window design, particularly in

(*Continued on page* 125)



*Modern American crystal jar with leaping faun engraving—by Libbey. A fine example of the modern glassmaker's skill.*

Regardless of the form that it takes, glass manufactured today is designed to meet high standards of both beauty and practical durability.

And leading glassmakers of today find Mathieson Dense Soda Ash especially fitted to meet these high standards. Its granular, uniform character secures quick, efficient melting . . . guarantees uniformity in the finished glass. It is free from large particles, dust or foreign matter that affect the quality of the glass. Let us quote on your dense soda ash requirements.

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**Dense Soda Ash**

THE MATHIESON ALKALI WORKS (INC.) 60 E. 42ND ST., NEW YORK, N. Y.

SODA ASH . . . CAUSTIC SODA . . . BICARBONATE OF SODA . . . LIQUID CHLORINE . . . BLEACHING POWDER . . . HTH PRODUCTS . . . AMMONIA, ANHYDROUS and AQUA . . . FUSED ALKALI PRODUCTS . . . SYNTHETIC SALT CAKE . . . DRY ICE . . . CARBONIC GAS . . . SODIUM CHLORITE PRODUCTS

# CURRENT PRICES OF GLASS-MAKING MATERIALS

**FURNISHED BY PRODUCERS, MANUFACTURERS AND DEALERS**

## Base Materials

| | | Carlots | Less Carlots |
|---|---|---|---|
| Barium carbonate ($BaCO_3$), Crude, (Witherite) 90%, 99% through 200 mesh | ton | 43.00 | 46.00-49.00 |
| Reduction on precipitated material, $5.00 a ton | | 45.00 | 50.00 |
| Barium sulphate, in bags | ton | 19.00 | 24.00 |
| Barium sulphate, glassmaker's, carlots, bulk f. o. b. shipping point | ton | 15.00-16.00 | 18.00 |
| Borax ($Na_2B_4O_7 10H_2O$) | lb. | .... | .... |
| Granulated | In bags, lb. | .0215 | .027 -.0295 |
| Powdered | In bags, lb. | .024 | .0295-.032 |
| Boric acid ($H_3BO_3$) granulated | In bags, lb. | .048 | .054 - .0565 |
| Calcium phosphate ($Ca_3(PO_4)_2$) | lb. | .07 | .07½ |
| Cryolite ($Na_3Al\ F_6$) Natural Greenland (Kryolith) | lb. | .0865-.0875 | .0925 |
| Synthetic (Artificial) | lb. | No supplies available. | |
| Feldspar—(published list prices) | | | |
| 20 mesh | ton | 11.00-13.25 | |
| 40 mesh | ton | 11.50-13.75 | |
| Granular | ton | 11.75-14.00 | |
| Semi-granular | ton | 11.00-13.25 | |
| L. C. L., (Min. 2 tons) $3.00 per ton additional plus charge for bags | | | |
| Fluorspar ($CaF_2$) domestic, ground, 96-98% (max $SiO_2$, 2½%) | | | |
| Bulk, carloads, f. o. b. mines | ton | 29.00 | .... |
| In bags | ton | 30.60 | 40.00-42.50 |
| Kryolith (see Cryolite) | | | |
| Lead Oxide ($Pb_3O_4$) (red lead) (N. Y.) | lb. | .0815 | .... |
| In 5 Ton lots | lb. | .... | .085 |
| Less than 5 Tons | lb. | .... | .09 |
| Lime— | | | |
| Hydrated ($Ca(OH)_2$-MgO) (in paper sacks) | ton | 8.50 | 8.50 |
| Burnt (CaO-MgO) ground, in bulk | ton | 7.00 | .... |
| Burnt, ground, in paper sacks | ton | 9.00 | 9.00 |
| Burnt, ground, in 180 lb. drums | Per drum | 1.60 | 1.70 |
| Kiln Dried ($CaCO_3$-$MgCO_3$) 10x30 mesh | ton | 1.75 | .... |
| Kiln Dried ($CaCO_3$-$MgCO_3$) 16x120 mesh. | ton | 1.75 | .... |
| Nepheline Syenite, f. o. b. shipping point | ton | 12.00 | 15.00 |
| Potassium carbonate— | | | |
| Calcined ($K_2CO_3$) 96-98% | lb. | .065 | .0675 |
| Hydrated 80-85% | lb. | .055 | .0575 |
| Salt cake, glassmakers ($Na_2SO_4$) in bags | ton | 18.00-20.00 | 25.00 |
| in bulk | | 16.50 | |
| Soda ash ($Na_2CO_3$) dense, 58%— | | | |
| Bulk | Flat Per 100 lb | .95 | .... |
| In barrels | Per 100 lb. | 1.35 | .... |
| In bags | Per 100 lb. | 1.10 | .... |
| Sodium nitrate ($NaNO_3$)— | | | |
| Refined (gran.) in bbls | Per 100 lb. | .... | 2.50-2.90 |
| 95% and 97% | | | |
| Bulk | Per 100 lb. | 1.35 | .... |
| 200 lb. bags | | 1.44 | 1.465 |
| 100 lb. bags | | 1.475 | 1.50 |

## Special Materials

| | | Carlots | Less Carlots |
|---|---|---|---|
| Aluminum hydrate ($Al(OH)_3$) | lb. | .026-.029 | .04 |
| Aluminum oxide ($Al_2O_3$) | lb. | .07 | .09 |
| Antimony oxide ($Sb_2O_3$) | lb. | .13 | .13½ |
| Arsenic trioxide ($As_2O_3$) (dense white) 99% | lb. | .03½ | .04 |
| Barium nitrate ($Ba(NO_3)_2$) | lb. | .... | Open price. |
| Pyrophyllite, (20% $Al_2O_3$) | ton | 9.00 | 12.00 |
| Sodium fluosilicate ($Na_2SiF_6$) | lb. | .... | |
| Tin Oxide ($SnO_2$) in bbls | lb. | .... | Open price. |
| Titanium Oxide (ceramic grade) | | | |
| In bags | lb. | .13 | .13¼-.13¾ |
| In barrels | lb. | .13¼ | .13½-.14 |
| Zinc Oxide (ZnO) | | | |
| American process, Bags | lb. | .06½ | .06¾ |
| White Seal, 150 lb. bbls | lb. | .09 | .09¼ |
| Green Seal bags | lb. | .08¼ | .08½ |
| Domestic White Seal bags | lb. | .08¾ | .09 |
| Red Seal, bags | lb. | .07¾ | .08 |
| Zircon | | | |
| Refined Granular (Milled .01-.02c higher) | | .06½ | 07-.08 |

## Coloring Materials

| | | Carlots | Less Carlot |
|---|---|---|---|
| Barium selenite ($BaSeO_3$) | lb. | .... | 1.40-1.60 |
| (Commercial, 25% Selenium) | lb. | .... | .85 |
| Cadmium sulphide (CdS) | lb. | .... | 1.05-1.10 |
| Cerium hydrate— | | | |
| 100 lb. drums and 600 lb. barrels | lb. | .... | .60 |
| Chrome Oxide Green, 400 lb. bbls. | lb. | .... | .22-.25 |
| Chromite (99% through 200 mesh) | ton | 45.00 | 48.50 |
| Chromite ore (air floated) | ton | 55.00 | 58.00-73.00 |
| Cobalt oxide ($Co_2O_3$) | | | |
| In bbls. 350 lbs. or more, | lb. | .... | 1.84 |
| Less than 350 lbs., | lb. | .... | 1.94 |
| Copper oxide— | | | |
| Red ($Cu_2O$) | lb. | .... | .165 |
| Black (CuO) | lb. | .... | .18-.19 |
| Black prepared | lb. | .... | .22 |
| Iron Oxide— | | | |
| Red ($Fe_2O_3$) | lb. | .... | .05-.09½ |
| Black ($Fe_3O_4$) | lb. | .04½ | .09 |
| Iron Chromate | lb. | .... | .035-.05 |
| Lead Chromate ($PbCrO_4$) in bbls. | lb. | .... | .135 |
| Lithium Carbonate | lb. | .... | 1.25 |
| Manganese, Black Oxide (Caucasian) | | | |
| In Paper bags | ton | 70.00 | 78.00 |
| In Burlap bags | ton | 71.75 | 79.75 |
| In Casks | ton | 74.00 | 82.00 |
| Neodymium oxalate, 50 lb. drums | lb. | .... | 4.00 |
| Nickel oxide ($Ni_2O_3$), black | lb. | .... | .35-.40 |
| Nickel monoxide (NiO), green | lb. | .... | .35-.37 |
| Potassium bichromate ($K_2Cr_2O_7$)— | | | |
| Crystals and Granular | lb. | .08¾ | .09-.09¼ |
| Powdered | lb. | .... | .09¼-.09¾ |
| Potassium Chromate ($K_2CrO_4$) 100 lb. kegs | lb. | .... | .27 |
| Powder blue | lb. | .... | .21-.25 |
| Rare earth hydrate— | | | |
| 100 lb. drums | lb. | .... | .35 |
| 325 lb. barrels | lb. | .... | .30 |
| Selenium (Se) In 100 lb. lots | lb. | .... | 1.75 |
| In lesser quantities | lb. | .... | 1.85 |
| Sodium bichromate ($Na_2Cr_2O_7$) | lb. | .06¾ | .07-.07¼ |
| Sodium chromate ($Na_2CrO_4$) Anhydrous | lb. | .08½ | .08½-.08⅝ |
| Sodium selenite ($Na_2SeO_3$) | lb. | .... | 1.50-1.65 |
| Sodium uranate ($Na_2UO_4$) Orange | lb. | .... | 1.65 |
| Yellow | lb. | .... | 1.65 |
| Sulphur (S)— | | | |
| Flowers, in bbls | Per 100 lb. | 3.35 | 3.70-4.10 |
| Flowers, in bags | Per 100 lb. | 3.00 | 3.35-3.75 |
| Flour, heavy, in 250 lb. bbls. | Per 100 lb. | 2.90 | 3.25-3.65 |
| Uranium oxide ($UO_2$) (black, 96% $U_3O_8$) 100 lb. lots. Black | lb. | .... | 2.55 |
| Yellow orange | lb. | .... | 1.65 |

## Polishing Materials

| | | Carlots | Less Carlots |
|---|---|---|---|
| Emery, Turkish | lb. | .063 | .07 |
| Pumice Stone, | | | |
| American Ground Italian FFF, FF, F | lb. | .... } open | |
| 0, 0½, ½, 1. | lb. | .... } price | |
| Putty Powder | lb. | Open price. | |
| Rotten Stone, (Domestic) | lb. | 02¼ | .03½ |
| Rouge, Red | lb. | .... | .16 |
| Black | lb. | .... | .18 |

## STAINED GLASS

(*Continued from page* 122)

domestic architecture, some notably fine windows have been done without lead lines, with the simple use of trace lines, shading and silver stain. I believe this modification of an old technique will, in time, demonstrate its value.

The third and last example bears on the possible treatments of glass block. Glass block has, I believe, come to stay. It has proven itself as a competent building material, but it is definitely subject to refinements. All attempts to color the whole block either from within or in its fabric have seemed to be in vain because of the coarseness of scale. The application of the glass-painter's materials and technique to the glass block do, however, give great promise. It seems that any color, pattern, design or mural can be applied to the block and fired on, as you would to tile. It is thus permanent. The enamels are protected from temperature changes and, thus, are reliable. Opacity is subject to control as well as color and, with this in mind, we find quite a new property in the glass wall. At night the opaque treatment serves to give substance to the wall, as well as continuity. The glass block wall ceases to be a black hole in the room. It actually has substance and tends to preserve the continuity of the surface.

## THERMAL EXPANSION OF GLASS

(*Continued from page* 115)

For a system like soda-silica glasses, the relationship between volume and composition has been well established and the idea of using volume percentages may be applied. We should like to mention that in the calculation of specific volumes of glass from the composition, Winkelmann and Schott's formula is justified in using weight percentages.

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††An important paper on the calculation of thermal expansion of glass from compositions has recently come to the attention of the authors, but too late for inclusion in Table II. The data to be inserted before the column "Gilard & Dubrul" in Table II is as follows:

| | Rencker[20] |
|---|---|
| $SiO_2$ | 2 |
| $Al_2O_3$ | —3 |
| BeO | 2 |
| MgO | 1 |
| CaO | 10 |
| ZnO | 4 |
| $Na_2O$ | 37 |

It is interesting to note that the factor for alumina is also negative.

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*Contribution Number 422 from the Department of Chemistry, University of Pittsburgh.

The authors wish to thank Messrs. E. H. McClelland and M. Schrero of the Carnegie Library of Pittsburgh for their help in the preparation of this paper.

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**SULFATES IN GLASS**
(*Continued from page* 113)

**Effect on Decolorizers**

Horak[57] concluded that the effect of sulfates is to decrease color due to selenium, but that if barium sulfate is used, the resulting barium oxide had a tendency to offset this decrease in color. Noel[30] stated that his experimental evidence showed a decreased selenium requirement when ammonium sulfate was used. Turner[58] contradicted Noel's statement, and suggested that more selenium was required when more than 7.5 parts of ammonium sulfate per 1000 parts of sand was used, due to the fact that the escaping ammonia kept the batch open, and facilitated the escape of selenium. He advised that the loss could be reduced by the use of selenites in place of selenium.

**Surface Effects**

Kitaigorodskii and Shlolnikov[59] found that gas containing $SO_2$ reacts with the surface of solid, hot glass, to form sulfates with the alkalies in the glass. The reaction is proportional to time, temperature, concentration of the $SO_2$ and the amount of alkali in the glass. Weyl and Pincus[46] stated that the effect of $SO_2$ on glass at the annealing temperature is to combine with the alkalies at the surface, resulting in sulfate conversion which increases with increasing alkali concentration in the glass. Menerey[60] attempted to prevent the bloom on ware in the lehr, by the removal of organic sulfur from city gas. Guss[61] concluded that the efforescence appearing on glass surfaces during annealing was due to the attack by lehr atmosphere containing $SO_2$ and $CO_2$, forming sulfates and carbonates on the glass surface. Hovestadt[62] states that the sulfates formed on glass during annealing may be easily washed off.

**Conclusions**

Sulfates have a definite place as raw materials in the manufacture of commercial glasses. Under properly controlled conditions, they are an aid in the melting and fining of glass. Due to their effect on viscosity, sulfates can be employed advantageously in the control of the working properties of glass. In general, the properties of the finished glass are benefited by the presence of dissolved sulfur trioxide, resulting mainly from undecomposed sulfates. There appears to be a limit to the amount of sulfate that can be introduced in a glass, under normal conditions, without the addition of a reducing agent to prevent the formation of "salt water" gall. Certain of the sulfates apparently exert a greater influence on the melting, fining, and properties of glass, than do others. Commercial practice in recent years has partially replaced salt cake, sodium sulfate, with other sulfates. Notable among these are ammonium sulfate and barium sulfate.

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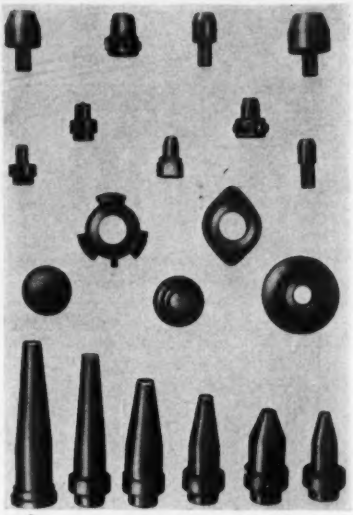

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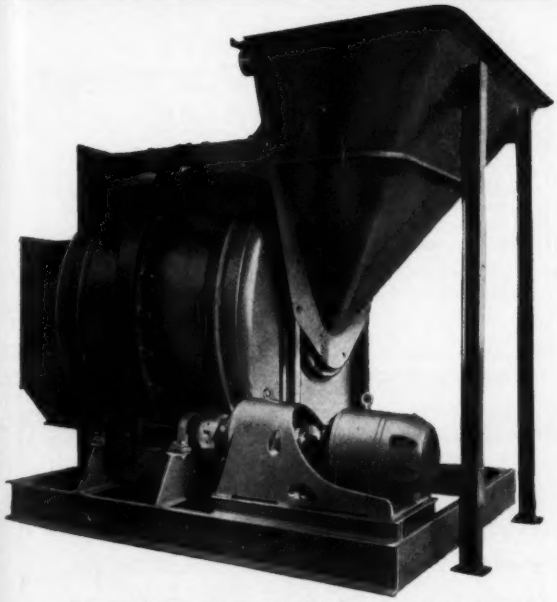

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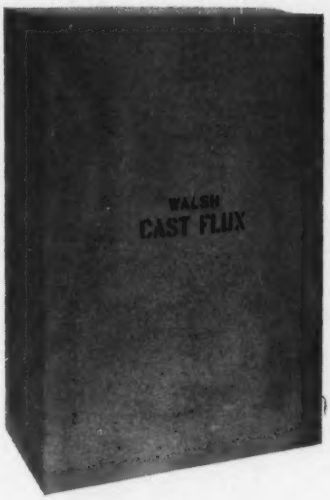
"IF IT'S MADE OF GLASS, ASK US FIRST"

# WALSH CAST-FLUX




**The Vacuum-cast flux block of superior quality.**

**Walsh Cast-Flux blocks are machine-trued to exact size and shape after burning.**

## THEY LAST LONGER

The excellent results obtained in numerous tanks melting various types of glass has definitely established the efficiency and economy of Walsh Cast-Flux blocks.

Walsh Cast-Flux has a dense, uniform structure; it is burned at higher temperatures, is thoroughly bonded and possesses a low coefficient of expansion.

Walsh Cast-Flux blocks meet the most rigid requirements for tanks operating at higher temperatures . . . they insure greater tonnage, higher quality glass, freedom from defects, longer life and maximum economy.

## WALSH REFRACTORIES CORPORATION

Manufacturers of Refractories for the glass industry for over 50 years

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